Supporting Information: "Enhanced dielectric permittivity of hierarchically double-gyroid nanocomposites via macromolecular engineering of block copolymers"

Zhanwen Xu,[†] Qingshu Dong,[†] Liangshun Zhang,^{*,‡} and Weihua Li^{*,†}

†State Key Laboratory of Molecular Engineering of Polymers, Key Laboratory of Computational Physical Sciences, Department of Macromolecular Science, Fudan University, Shanghai 200433, China

‡Shanghai Key Laboratory of Advanced Polymeric Materials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

E-mail: zhangls@ecust.edu.cn; weihuali@fudan.edu.cn

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Self-Consistent Field Theory Coupled with Density Functional Theory (SCFT/DFT)

The method coupling self-consistent field theory and density functional theory for the mixture consisting of block copolymers and nanoparticles was developed by Balazs and coworkers, which is based on the mean-field approximation.^{S1} We consider a mixture of volume *V* consisting of melting $A'(A''B)_n$ miktoarm star block copolymers and solid spherical nanoparticles. All nanoparticles have the same radius R_P , and their concentration is denoted as ψ_P . Each copolymer chain is modeled as a flexible Gaussian chain containing *N* segments of volume ρ_0^{-1} and length *a*.

The free energy functional of the blending system in the SCFT/DFT model is expressed as

$$\frac{NF}{\rho_{0}k_{B}TV} = -(1-\psi_{P})\ln\frac{Q_{C}}{V(1-\psi_{P})} - \frac{\psi_{P}}{\alpha}\ln\frac{\alpha Q_{P}}{V\psi_{P}} + \frac{1}{V}\int d\mathbf{r}$$

$$\left[\frac{1}{2}\sum_{\mu,\nu=A,B,P;\mu\neq\nu}\chi_{\mu\nu}N\phi_{\mu}\left(\mathbf{r}\right)\phi_{\nu}\left(\mathbf{r}\right) - \sum_{\mu=A,B}w_{\mu}\left(\mathbf{r}\right)\phi_{\mu}\left(\mathbf{r}\right) - w_{P}\left(\mathbf{r}\right)\rho_{P}\left(\mathbf{r}\right)\right] \quad (S1)$$

$$+ \frac{1}{V}\int d\mathbf{r}\rho_{P}\left(\mathbf{r}\right)\Psi_{HS}\left(\bar{\phi}_{P}\left(\mathbf{r}\right)\right),$$

where k_B is the Boltzmann constant and T is the temperature. α is the volume ratio of the nanoparticle with radius R_P to the block copolymer chain, i.e., $\alpha = 4\pi R_P^3/3N\rho_0^{-1}$. $\chi_{\mu\nu}$ characterizes the interaction between species μ and ν . $\phi_A(\mathbf{r})$, $\phi_B(\mathbf{r})$ and $\phi_P(\mathbf{r})$ are the spatial distribution of volume fractions of A block, B block and nanoparticles, respectively, while $w_A(\mathbf{r})$, $w_B(\mathbf{r})$ and $w_P(\mathbf{r})$ are their conjugate potential fields. $\rho_P(\mathbf{r})$ is the density distribution of nanoparticles. The local volume fraction of nanoparticles $\phi_P(\mathbf{r})$ is related to the density distribution $\rho_P(\mathbf{r})$ by the local integration $\phi_P(\mathbf{r}) = (3\alpha)/(4\pi R_P^3) \int_{|\mathbf{r}'| \le R_P} d\mathbf{r}' \rho_P(\mathbf{r} + \mathbf{r}')$. Q_P is the partition function for single nanoparticle under the field $w_P(\mathbf{r})$, and is given by $Q_P = \int d\mathbf{r} \exp(-w_P(\mathbf{r}))$.

 A'/A" junction point indicated by s = 0 and the A"/B junction point indicated by $s = (f - f_{A'})/n$ with the initial conditions as $q_{A''}(\mathbf{r}, 0) = q_{A'}(\mathbf{r}, f_{A'}) \left[q_{A''}^{\dagger}(\mathbf{r}, 0)\right]^{n-1}$ and $q_{A''}^{\dagger}(\mathbf{r}, (f - f_{A'})/n) = q_B^{\dagger}(\mathbf{r}, 0)$, respectively. For each B-block, $q_B(\mathbf{r}, s)$ and $q_B^{\dagger}(\mathbf{r}, s)$ start from the A"/B junction point indicated by s = 0 and its free end indicated by s = (1 - f)/n with the initial conditions as $q_B(\mathbf{r}, 0) = q_{A''}(\mathbf{r}, (f - f_{A'})/n)$ and $q_B^{\dagger}(\mathbf{r}, (1 - f)/n) = 1$, respectively. The two categories of propagator functions satisfy the following modified diffusion equations

$$\frac{\partial}{\partial s} q_K(\mathbf{r}, s) = \nabla^2 q_K(\mathbf{r}, s) - w(\mathbf{r}) q_K(\mathbf{r}, s), \qquad (S2)$$

$$-\frac{\partial}{\partial s}q_{K}^{\dagger}(\mathbf{r},s) = \nabla^{2}q_{K}^{\dagger}(\mathbf{r},s) - w(\mathbf{r})q_{K}^{\dagger}(\mathbf{r},s), \qquad (S3)$$

where $w(\mathbf{r}) = w_A(\mathbf{r})$ for K = A' and A'', and otherwise $w(\mathbf{r}) = w_B(\mathbf{r})$. The above equations imply that the chain contour is rescaled by N, and the length unit chosen as $R_g = N^{1/2} a / \sqrt{6}$ where a is the Kuhn length of A and B blocks.

The last term of eq S1 describes the steric free energy of the particles according to Carnahan-Starling function $\Psi_{HS}(x) = (4x - 3x^2)/((1 - x)^2)$.^{S2} $\bar{\phi}_P(\mathbf{r})$ is the weighted nonlocal volume fraction of particles. The relationship between $\bar{\phi}_P(\mathbf{r})$ and $\rho_P(\mathbf{r})$ is as follows:

$$\bar{\phi}_P(\mathbf{r}) = (3\alpha)/(4\pi (2R_P)^3) \int_{|\mathbf{r}'| \le 2R_P} d\mathbf{r}' \rho_P(\mathbf{r} + \mathbf{r}').$$
(S4)

Minimization to the free energy functional in eq S1 leads to the following set of self-consistent equations:

$$w_{A}(\mathbf{r}) = \chi_{AB} N \phi_{B}(\mathbf{r}) + \chi_{AP} N \phi_{P}(\mathbf{r}) + \xi(\mathbf{r}), \qquad (S5)$$

$$w_B(\mathbf{r}) = \chi_{AB} N \phi_A(\mathbf{r}) + \chi_{BP} N \phi_P(\mathbf{r}) + \xi(\mathbf{r}), \qquad (S6)$$

$$w_{P}(\mathbf{r}) = \Psi_{HS}\left(\bar{\phi}_{P}(\mathbf{r})\right) + \frac{3\alpha}{4\pi(2R_{P})^{3}} \int_{|\mathbf{r}'| \leq 2R_{P}} d\mathbf{r}' \rho_{P}(\mathbf{r} + \mathbf{r}') \Psi'_{HS}\left(\bar{\phi}_{P}(\mathbf{r} + \mathbf{r}')\right) + \frac{3\alpha}{4\pi R_{P}^{3}} \int_{|\mathbf{r}'| \leq R_{P}} d\mathbf{r}' \left[\chi_{AP} N \phi_{A}(\mathbf{r} + \mathbf{r}') + \chi_{BP} N \phi_{B}(\mathbf{r} + \mathbf{r}') + \xi(\mathbf{r} + \mathbf{r}')\right],$$
(S7)

Where

$$\Psi'_{HS}(x) = \frac{\mathrm{d}\Psi_{HS}(x)}{\mathrm{d}x},\tag{S8}$$

$$\phi_{A}(\mathbf{r}) = \frac{(1 - \psi_{P})V}{Q_{C}} \left[\int_{0}^{f_{A'}} q_{A'}(\mathbf{r}, s) q_{A'}^{\dagger}(\mathbf{r}, s) ds + n \int_{0}^{(f - f_{A'})/n} q_{A''}(\mathbf{r}, s) q_{A''}^{\dagger}(\mathbf{r}, s) ds \right],$$
(S9)

$$\phi_B(\mathbf{r}) = \frac{n(1-\psi_P)V}{Q_C} \int_0^{(1-f)/n} q_B(\mathbf{r}, s) q_B^{\dagger}(\mathbf{r}, s) \,\mathrm{d}s, \qquad (S10)$$

$$\rho_P(\mathbf{r}) = \frac{\psi_P V}{\alpha Q_P} \exp\left(-w_P(\mathbf{r})\right). \tag{S11}$$

The spatial function $\xi(\mathbf{r})$ is a Lagrange multiplier function used to enforcing the incompressibility condition $\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) + \phi_P(\mathbf{r}) = 1$. These SCFT equations are solved iteratively by the pseudospectral method.^{S3}

Finite Difference Quasielectrostatic Modeling for Determining the Dielectric Properties

The calculation of the effective permittivity for the polymer/nanoparticle mixture is based on a quasielectrostatic finite-difference formulation.^{S4} Such quasistatic methods are useful for simulating systems in which the characteristic structure sizes are much smaller than the electromagnetic wavelength.

We consider a parallel plate capacitor filled by the mixture of $A'(A''B)_n$ miktoarm star block copolymers and nanoparticles forming the G structure. In the plate capacitor, a constant potential difference $U_0 = U_{up} - U_{down}$ is kept between the capacitor plates. Once the model space is filled with the desired arrangement of constituent phases, the potentials at the grid points can be obtained by the continuity of electric displacement,

$$\nabla \cdot \left[\boldsymbol{\varepsilon} \left(\mathbf{r} \right) \mathbf{E} \left(\mathbf{r} \right) \right] = 0, \tag{S12}$$

where $\mathbf{E}(\mathbf{r})$ is the electric field, and $\boldsymbol{\varepsilon}(\mathbf{r})$ is the permittivity at position \mathbf{r} . The electric fields for this step are computed from the differences between the potentials at neighboring grid points. Bi-conjugate gradient technique is employed to accelerate convergence. After the system has been converged, the electric field distribution throughout the model space is computed from the gradients of the potentials. Then, the effective permittivity, $\boldsymbol{\varepsilon}_{\text{eff}}$, can be calculated via

$$\varepsilon_{\rm eff} = \frac{h \int_{\Omega} \varepsilon(\mathbf{r}) \mathbf{E}(\mathbf{r}) \cdot \mathbf{dS}}{S \left(U_{\rm up} - U_{\rm down} \right)},\tag{S13}$$

where the *h* and *S* are the thickness and surface area of the capacitor. The integral in Equation S12 extends over the surface Ω of the capacitor.

The local permittivity $\varepsilon(\mathbf{r})$ is determined according to the distribution of the different components in the self-assembled structures of the mixing $A'(A''B)_n$ copolymers and nanoparticles. Since the organization of the nanoparticles is a critical factor affecting the dielectric properties, we map the density distribution of nanoparticles obtained from the SCFT/DFT method into the positions of the particle centers by using the density-biased Monte Carlo method. The mapping process is shown in Figure S9a. After the mapping process, each grid in the calculation space is occupied by nanoparticles or block copolymers, and the permittivity is $\varepsilon_{NP} = 1235$ or $\varepsilon_{poly} = 3.6$ at nanoparticle or copolymer occupying grids.

The density-biased Monte Carlo method can lead to deviations in the calculated equivalent permittivity between different mappings. Therefore, the effective macroscopic permittivity is obtained by averaging over a larger number of mappings. It is found that the average permittivity converges to almost constant over 200 mappings (see Figure S9b).



Figure S1: (a) Phase diagram with respect to f and τ for the pure A'(A''B)₃ copolymer. (b) Width of the gyroid region as a function of τ .



Figure S2: Phase diagram with respect to *f* and ψ_P for the AB diblock copolymer/nanoparticle mixture with $\chi_{AB}N = \chi_{BP}N = 35$ and $\chi_{AP}N = 0$.



Figure S3: One-dimensional distributions of nanoparticles, A' and A''-blocks in the cylinder morphology (C₆) at fixed f = 0.45 and $\tau = 0.72$ for various ψ_P : (a) $\psi_P = 0.025$, (b) $\psi_P = 0.075$, (c) $\psi_P = 0.125$ and (d) $\psi_P = 0.175$.



Figure S4: Phase diagrams with respect to the effective volume fraction f_{eff} and ψ_P of the A'(A''B)₃/NP mixture with $\chi_{AB}N = \chi_{BP}N = 35$ and $\chi_{AP}N = 0$: (a) $\tau = 0.72$, (b) $\tau = 0.6$, (c) $\tau = 0.2$ and (d) $\tau = 0.8$.



Figure S5: Phase diagrams with respect to f and ψ_P for A'(A''B)₃/NP mixtures with $\chi_{AB}N = \chi_{BP}N = 35$ and $\chi_{AP}N = 35$ for $\tau = 0$ (a) and $\tau = 1$ (b).



Figure S6: (a) Width of the G-phase region of the A'(A"B)₃/NP mixture as a function of τ at fixed $\psi_P = 0.1$ and $R_P = 0.5R_g$ for $\chi_{AB}N = 35$, $\chi_{AB}N = 40$, $\chi_{AB}N = 50$ and $\chi_{AB}N = 60$. (b) Width of the G-phase region as a function of τ at fixed $\psi_P = 0.1$ and $\chi_{AB}N = 35$ for $R_P = 0.3R_g$, $R_P = 0.4R_g$, $R_P = 0.5R_g$ and $R_P = 0.6R_g$.



Figure S7: Channel size (a) and effective concentration $\psi_{P,eff}$ of nanoparticles within the channels (b) of the double-gyroid structure as a function of ψ_P for $\tau = 0.6$ and f = 0.5. Channel size (c) and $\psi_{P,eff}$ (d) as a function of f for $\psi_P = 0.15$.



Figure S8: (a) The dimension of the unit cell of the double-gyroid structure l_0 as a function of ψ_P for f = 0.5 and $\tau = 0.6$. (b) l_0 as a function of f for $\psi_P = 0.15$ and $\tau = 0.6$.



Figure S9: (a) Schematic illustration of the mapping process by using the density-biased Monte Carlo method. (b) Averaged permittivity as a function of the number of repeated mappings.

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