

Functionalized Polymers as Templates for Nanoparticle Self-Assembly

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We consider a solution of triblock copolymers forming a hexagonal phase of micelles and investigate the effect of adding attractive particles. Our results show that if the triblock is functionalized at its ends by attaching groups with specific affinity for the particles, the system self-assembles into new phases where the particles crystallize following the mesoscopic order imposed by the polymeric matrix, which serves as a template. Examples of different lamellar and gyroid phases (both with $Ia\bar{3}d$ and $I4_132$ space symmetry) are presented in detail. We briefly discuss the implications for polymer templating of nanoparticles or inorganic crystals.

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The fascinatingly rich phase diagram of block copolymer solutions and melts [1, 2] is vastly expanded when combined with inorganic components such as nanoparticles. A very interesting possibility is the crystallization of an inorganic component so that it follows the mesoscopic order imposed by the polymeric phase, which serves as a template. These polymer nanocomposite crystals offer huge possibilities for new materials with exquisitely tuned optical, mechanical or transport properties.

Multiblock copolymers containing both hydrophilic and hydrophobic blocks are particularly suitable as templates, as they generally aggregate into micelles whose geometry and structure can be tightly controlled by varying the hydrophobic/hydrophilic ratio or by external conditions such as temperature or pH. A pertinent example is provided by Pluronic or poloxamer polymers, short symmetric triblocks (ABA) where the B-block is polypropylene oxide (PPO) and the A-block is polyethylene oxide (PEO). Pluronic are particularly versatile as templates, as they exhibit a myriad of phases over narrow temperature and concentration regions [1].

In this letter, we investigate concrete conditions leading to successful templating by considering a generic ABA triblock coexisting with inorganic particles, which herein will be referred to as nanoparticles. We assume that nanoparticles aggregate, and therefore attract each other with a characteristic energy ε_N (see Fig. 1). In the absence of any specific interaction between polymer and nanoparticles, successful templating can only occur if the polymeric phase is able to coerce nanoparticle aggregation and direct it towards the regions occupied by the solvent. An alternative templating strategy may be achieved by functionalizing the polymer end blocks by covalently attaching a group with high affinity for the nanoparticles (see Fig. 1). In this way, the end groups provide multiple centers for nucleating the aggregation of the inorganic phase, possibly inducing a uniform growth from the polymeric template. Functionalization is modelled by introducing an energy scale ε_F , the energy gain for nanoparticles to bind to the functionalized group. Experimentally, methods for functionalizing polymers are available, and there is a considerable repertoire of groups

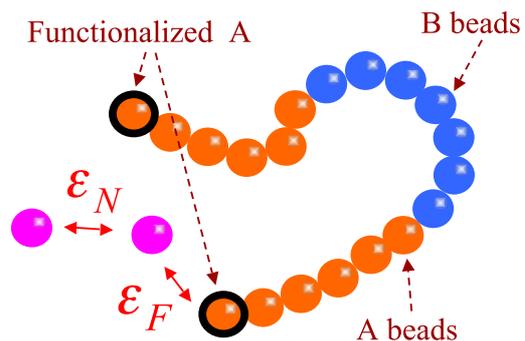


FIG. 1: (Color Online:) Schematic representation of the system considered. An ABA triblock (A=6, B=7) functionalized polymer. The nanoparticles are single beads that attract each other with characteristic energy ε_N , and with an energy ε_F to the functionalized A-beads.

that can be attached, for example, to Pluronic [3].

We model a generic Pluronic, such that the pure system forms a hexagonal phase. In this paper, we consider an $A_6B_7A_6$ polymer. The nanoparticles are modelled as single beads (see Fig. 1). The interactions follow from Ref. [4]. The solvent is considered implicitly and the non-bonded potentials are described according to

$$V(r) = 4\varepsilon_{IJ} \left[\left(\frac{\sigma}{r} \right)^{12} - \alpha_{IJ} \left(\frac{\sigma}{r} \right)^6 \right]. \quad (1)$$

B-beads are hydrophobic while A-beads are hydrophilic $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{AB} \equiv \varepsilon_P$ and $\alpha_{AA} = \alpha_{AB} = 0$, $\alpha_{BB} = 1$. Nanoparticle-polymer interactions are described by $\alpha_{NN} = \alpha_{NA,B} = 0$ and $\varepsilon_{NA} = \varepsilon_{NB} = \varepsilon_P$, while nanoparticle-nanoparticle interactions by $\varepsilon_N \equiv \varepsilon_{NN}$, which is a free parameter, and $\alpha_{NN} = 1$. Functionalized polymers are described by the same parameters except for the two end beads, given by $\varepsilon_F \equiv \varepsilon_{AN}$ (see Fig. 1), the second free parameter of the model, and $\alpha_{AN} = 1$.

All beads in our model have the same mass m and interaction range σ . Simulations are carried out with the LAMMPS simulations package [5]. A number N_{poly}

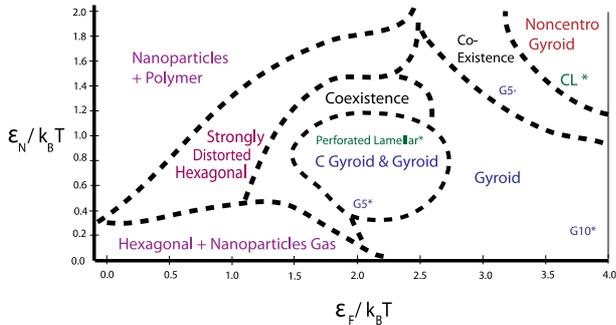


FIG. 2: (Color Online:) Phase Diagram as a function of nanoparticle-nanoparticle (ε_N) and nanoparticle-functionalized end (ε_F) interaction for a concentration of 5% polymers at $k_B T/\varepsilon_P = 1.2$. Phases with asterisks are expected to have a narrow stability range or be metastable.

of polymers are considered in a finite cube of length L (in units of σ) with periodic boundary conditions. The polymer packing fraction ϕ_P is related to L and N_{poly} by $\phi_P = \frac{\pi N_{\text{poly}} N_{\text{mon}}}{6L^3}$, where $N_{\text{mon}} = 19$ is the number of beads per polymer. The value of $\varepsilon_P/k_B T$ is fixed at 0.8333.

All results were obtained with a polymer fraction $\phi_P = 0.25$, where the $A_6B_7A_6$ polymer without nanoparticles is found in a hexagonal phase. The nanoparticle fraction was fixed at 5% (about two nanoparticles per functionalized group). The simulation runs took between 2–30 million steps, depending on the system size and the phase. In most cases, in order to ensure reproducibility, different initial configurations were tested. Additional technical details can be found in the auxiliary materials. Ordered structures are analyzed by computing the static structure factor

$$S_{JJ}(\mathbf{q}) = C_J \sum_{k=1} \sum_{l=1} \langle e^{i\mathbf{q}(\mathbf{r}_k^J - \mathbf{r}_l^J)} \rangle, \quad (2)$$

where $J = A, B$ or N refer to hydrophilic, hydrophobic or nanoparticle beads. C_J is chosen so that $S_{JJ}(\mathbf{0}) = 1$.

Simulations spanning system sizes between $N_{\text{poly}} = 400 - 3000$ were performed (see the auxiliary material for details). The most recurrent phases at various system sizes were considered thermodynamically stable. The phase diagram best summarizing all simulation results is shown in Fig. 2. Obviously, Phase boundaries cannot be determined with precision.

We first discuss non-functionalized polymers ($\varepsilon_F/k_B T \ll 1$). For weakly attracting nanoparticles ($\varepsilon_N/k_B T \ll 1$) thermal effects prevent nanoparticle aggregation and the micelles remain in the hexagonal phase while the nanoparticles are in a “gas” phase, freely diffusing within the solvent. As nanoparticle attraction is increased $\varepsilon_N/k_B T \sim 1$, nanoparticles eventually aggregate into a spherical blob (fluid or crystalline) as shown in Fig. 3(Left). The polymeric matrix is unable to template as the nanoparticles segregate from the

polymer phase (Nanoparticle+Polymer in Fig. 2).

In the weakly functionalized case $\varepsilon_F/k_B T \lesssim 1$, nanoparticles distort the polymeric matrix, which roughly maintains its hexagonal form. Interesting results occur for $\varepsilon_F/k_B T \gtrsim 2$; Here, the polymer matrix successfully templates the inorganic phase into different lamellar and gyroid phases (see Fig. 2) at the expense of the original hexagonal phase.

A snapshot of a perforated lamellar phase where the nanoparticles are successfully templated is shown in Fig. 3(Center). The perforations form a two dimensional hexagonal lattice (see Fig. 3(Right)). Quite remarkably, the lamellar planes and the perforations are uniformly covered with nanoparticles. The fact that the perforated lamellar phase was not found in all system sizes (see the auxiliary material) raises the possibility that is metastable or that its stability domain is narrow.

Gyroids are the most prevalent phases. Representative snapshots are shown in Fig. 4 and a typical structure factor confirming the gyroid structure is shown in Fig. 6(left). The nanoparticles show interesting variations in their structure. In Fig. 4(Center) it is shown that nanoparticles exhibit an almost perfect two dimensional curved surface, which we denote as a carpeted(C) gyroid, while in most other cases, a structure like the one in Fig. 4(Right) is found. The analysis of the structure factor Fig. 6(left) shows that both the nanoparticles and the hydrophobic blocks conform to the $Ia\bar{3}d$ symmetry, thus providing clear evidence for a successful templating. Occasionally, gyroids with structure factors showing peaks not allowed by the $Ia\bar{3}d$ symmetry, such as $\sqrt{5}$ and $\sqrt{10}$, indicated as G^5 and G^{10} in Fig. 2 are found, suggesting distortions due to a lattice constant incommensurate with the simulation box size, a point that will be elaborated elsewhere.

For strongly attracting nanoparticles and $\varepsilon_F/k_B T \gtrsim 3$, the unit cell of the gyroid becomes non-centrosymmetric, thus reducing the space group symmetry from $Ia\bar{3}d$ to $I4_132$. In Fig. 5(Center) a snapshot of the non-centrosymmetric gyroid is shown, where it is quite apparent that the simulation box contains two unit cells per linear dimension (8 in total). An analysis of the structure factor, Fig. 6(Right) confirms the $I4_132$ symmetry and the size of the unit cell. Also in this case, the nanoparticles exhibit the $I4_132$ symmetry, see Fig. 5(Right) for a snapshot, thus confirming a successful templating.

In the region where non-centrosymmetric gyroids are found, a new Checkerboard Lamellar (CL) phase was observed in some system sizes. The CL phase consists of lamellar planes, where each lamellar plane contains patches of nanoparticles and polymers, as shown in Fig. 5(Left). This phase, however, was not consistently found in all system sizes and it is possibly metastable.

The structure factor for the lamellar phases were also computed and showed the expected peaks (results not shown). Regions of the phase diagram that did not settle into definite phases are indicated as coexistence regions.

The goal of this letter was to investigate concrete

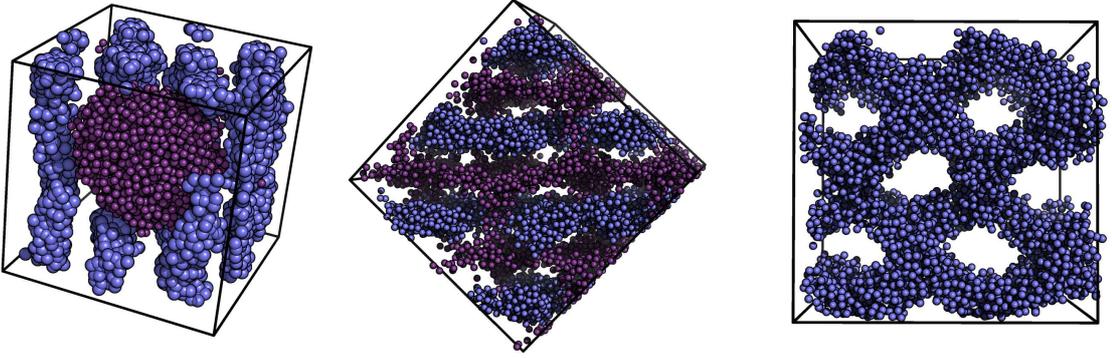


FIG. 3: (Color Online:) (Left) Snapshot of non-functionalized polymers and nanoparticles, an example of a failed template. (Center) Snapshot of the perforated lamellar, a successful nanoparticle templating (Right) snapshot of the perforated lamellar without the nanoparticles showing that the perforations form a hexagonal lattice. The B-beads are blue and nanoparticles purple. In all cases, the hydrophilic A-beads are omitted for clarity. All snapshots are created with PyMOL [6]

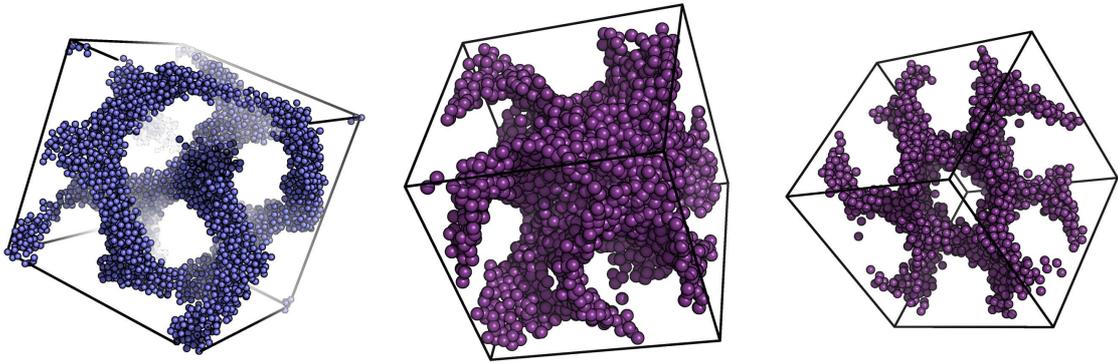


FIG. 4: (Color Online:) (Left) Snapshot of a gyroid (space group $Ia\bar{3}d$) where only B-beads are displayed. (Center) Example of the nanoparticles in a carpeted gyroid. (Right) Nanoparticles in a regular gyroid. In all cases, nanoparticles are ordered with the $Ia\bar{3}d$ space group.

strategies that lead to successful templating with multi-block polymers. A first, but we believe important result is that in the absence of specific interactions between polymer and nanoparticles, templating fails; The polymeric matrix is not rigid enough to direct the crystallization of the inorganic phase, see Fig. 3(Left).

Functionalization, however, does provide a successful templating strategy. As discussed, the crystalline polymeric matrix is able to direct the self-assembly of the inorganic phase into mesostructures displaying the same symmetry. Our results are significant in this respect, because to our knowledge, gyroid phases consisting of simple particles, which are predicted to exist in this paper, have not been reported before in the literature (see the structure factor for the nanoparticles in Fig. 6).

Gyroid phases are unusual and have been found in very few systems only, which we briefly discuss in connection with this work. In the $\varepsilon_N/k_B T \ll 1$ limit, the functionalized polymers may bind several nanoparticles, thus resembling tethered polymers, which also exhibit gyroid phases [7]. Our results suggest that tethered polymers with added hydrophobic blocks might enhance the range

of stability of the gyroid phase. Functionalized polymers keep the two end groups at the boundary of the micellar coronas, just like the phospholipid head groups in membranes, which show gyroid phases at large spontaneous curvature and relatively low water content [8]. In diblock melts, recent studies suggest a domain of stability for gyroid phases much broader than previously expected [9]. In Ref. [10, 11] it was argued that nanoparticles stabilize gyroid phases over a broader parameter space region by filling the gaps in the gyroid nodes. The mechanism that stabilizes the gyroid in our work is definitely different, but it remains as an interesting question how functionalization would affect the melt phase diagram, particularly in those regions where the gyroid is already stable.

In summary, we have shown that polymer functionalization provides an elegant route for templating inorganic crystals that exhibit mesoscopic order. Furthermore, our results strongly suggest that gyroids in functionalized polymer nanocomposites are ubiquitous when the pure polymer phase consists of cylindrical micelles, as will be elaborated elsewhere. There are many directions along which this work will be extended. This includes more

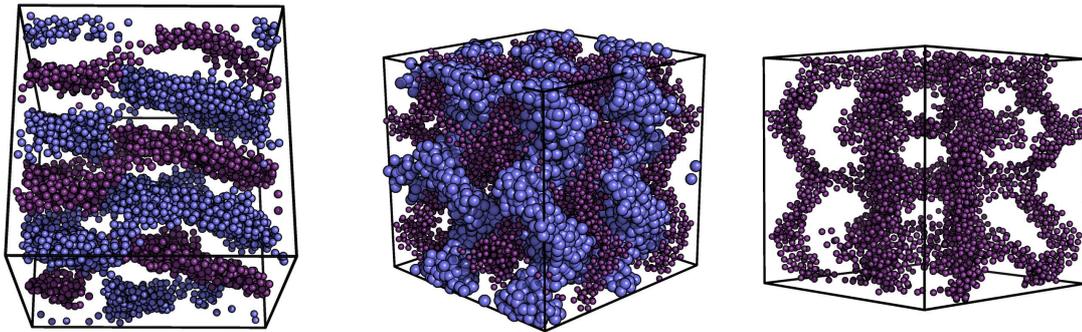


FIG. 5: (Color Online:) (Left) Snapshot of the checkerboard lamellar phase. (Center) Snapshot of the non-centrosymmetric gyroid (space group $I4_132$). (Right) Snapshot of the distribution of the nanoparticles in the non-centrosymmetric gyroid (also ordered with the $I4_132$ space group).

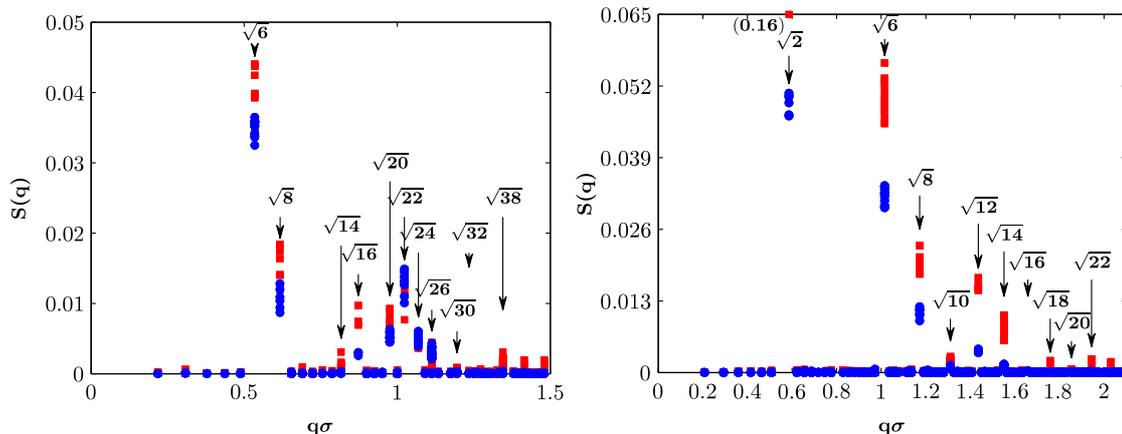


FIG. 6: (Color Online:) (Left) Structure factor of the gyroid ($N_{\text{poly}} = 600, \varepsilon_F/k_B T = 2.5, \varepsilon_N/k_B T = 1.0$) with space group $Ia\bar{3}d$ with the expected location of the peaks. (Right) Structure factor of the gyroid (700, 3.9, 1.8) with space group $I4_132$. The structure factor for nanoparticle beads is indicated by red squares while the one for the B-beads is shown with blue circles.

general multiblocks, nanoparticle types, functionalization protocols or branched polymers, which may stabilize phases with $Pm\bar{3}n$ symmetry [12]. Furthermore, we mention recent experiments where functionalized Pluronics have been used to template inorganic phases [13]. Multiblock solutions with gold, silver or silica nanoparticles may also provide interesting experimental realizations.

Acknowledgments

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