Topology and Shape Control for Assemblies of Block-Copolymer Blends in Solutions

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Abstract

We study binary blends of asymmetric diblock copolymers (AB/AC) in selective solvents with a meso-scale model. We investigate the morphological transitions induced by the concentration of the AC block copolymer and the difference in molecular weight between the AB and AC copolymers, when segments B and C exhibit hydrogen-bonding interactions. To the best of our knowledge, this is the first work modeling mixtures of block copolymers with large differences in molecular weight. The co-assembly mechanism localizes the AC molecules at the interface of A and B domains, and induces the swelling of the B-rich domains. The coil size of the large molecular weight block copolymer, depends only on the concentration of the short block copolymer (AC or AB), regardless of the B-C interactions. However, the B-C interactions control the morphological transitions that occur in these blends.

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Introduction

Amphiphilic diblock copolymers form self-assembled aggregates in the presence of selective solvents. A variety of morphologies have been extensively reported,¹⁻⁴ including, small spherical micelles, rods, large compound micelles, vesicles as well as bicontinuous structures. The local segregation of the AB blocks induces the characteristic shape and topology of the different morphologies. This segregation balances enthalpic and entropic interactions.

In nature, the self-assembly of amphiphilic molecules plays an important role during the formation of biological membranes. Remarkably, living organisms can modify morphological and mechanical properties of their membranes by blending different amphiphilic molecules.⁵ In cells for example, the rigidity of the membrane can be regulated dynamically varying the composition of different phospholipids. Inspired by this paradigm, amphiphilic block copolymer blends in selective solvents could be used to modify the properties of existent materials or design new materials with nano-scale resolution. The addition of a second block copolymer offers novel opportunities to combine multiple length-scale resolutions, enhance the mechanical properties, and increase the variety of morphologies and sizes of the assemblies.

Control of the co-assembly of block copolymer blends in selective solvents offers a large number of opportunities to fabricate new functional nano-structured materials^{6,7} with applications in pharmacology, catalysis, electronics, oil recovery, water purification, among many others. The shape and topology of self-assembled structures can be affected by changes in the molecular packing,⁸⁻¹³ and segregation kinetics^{3,14-16} (i.e., preparation method, initial polymer concentration, and transport of the polymer chains). Thermodynamically, the self-assembly of block copolymers (BCPs) can be described using the free energy G of the aggregates. For instance, the free energy of core-shell aggregates is typically approximated as $G = G_{\text{intf}} + G_{\text{core}} + G_{\text{shell}}$, where G_{intf} accounts for the formation of core-shell interfaces, whereas G_{core} and G_{shell} consider the core- and shell-forming block stretching from their unperturbed conditions. The interfacial energy contribution is consid-

ered proportional to the interfacial area A_{intf} , such that $G_{\text{intf}} \approx \gamma A_{\text{intf}}$, being γ the effective interfacial tension. In principle, we may expect that the thermodynamic state and mechanical properties exhibited by blends share features of their pure constitutive block copolymers.¹³ However, due to the competition between thermodynamic and kinetic effects, the characteristics forecast of the final aggregates is still cumbersome. Due to the complex behavior of block copolymer blends, forecasting their self-assembly and behavior is an area of research where experimental, theoretical, and computational studies are still scarce.

Some computational studies on self-assembly of block copolymer blends in solution have been reported in the last decade, including self-consistent-field theory (SCFT),^{11,15,17,18} Monte Carlo,^{19–23} Brownian Dynamics²⁴ and Dissipative Particle Dynamics.^{16,25–33} A number of publications focuses on block copolymer/homopolymer blends (AB/A and AB/C),^{20,31,34} block copolymers in small amounts as compatibilizers for homopolymer blends (AB/A/B, AB/A/C or AB/C/D).^{28,35} However, a significant part of the publications focus on melt and not solutions.^{36,37} Where in fact, an even larger variety of morphologies can be observed. As far as blends of two block copolymers are concerned, few reports are available. Focus has been on AB/AB copolymers with different molecular weights^{22,38} but less on AB/AC blends. AB/AC blends have been considered before, but only with similar molecular weights.^{16,23,32,39} In general the morphology prediction for block copolymer blends is complex, the available understanding of polymer blends is patchy and incomplete. For instance, the morphological transition process is unclear when a second diblock copolymer is co-assembled. That is, the impact of the presence of the AC molecules on the molecular-packing parameters and the segregation kinetics is not yet understood. Moreover, experimentally-relevant conditions such as large length ratios have not been explored computationally. Motivated by the insights derived from our previous experimental work,⁴⁰ herein we tackle these long-standing issues using dissipative particle dynamics (DPD),^{41–43} to model binary blends of AB/AC block copolymers in selective solvents. DPD is particularly suitable for semi-diluted conditions, a concentration range of relevance for applications like coatings and membrane manu-

facture.⁴⁴

We model binary blends constituted by high molecular weight $(AB)_{hi}$ and low molecular weight $(AC)_{lo}$ in a selective solvent for B. We vary the Flory-Huggins interaction parameter between the B and C blocks from zero to negative values ($\chi_{BC} < 0$), such that the interactions between the B and C monomers are modeled as an effective affinity between their respective coarse-graining representations. These affinity can be associated for instance with favorable hydrogen-bonding interactions. Previous results for BCP mixtures using Monte Carlo simulations²³ evidenced that directional dependency of hydrogen bonds modify the self assembly of BCPs. We remark that our DPD scheme only considers soft interactions between particles, and directional dependency or formation of hydrogen bonds cannot be explicitly modeled. Nevertheless, the generic affinity interactions that we use, allow us to model larger systems, compared to those where hydrogen-bond formation is explicitly accounted for. Similar approaches have been used in self-consistent-field methods.^{36,45}

For this selected set of systems, we investigate the changes in morphology due to the effect of the molar ratio $\phi = n_{AC}/n_{AB}$, the length ratio of the diblock copolymers $l_r = N_{AB}/N_{AC}$, and the preparation method, where n_i and N_i denote the number of moles and number of repetitive units of the i th block copolymer, respectively. Using the length and molar ratio we define the weight ratio as $\phi = m_{AC}/m_{AB} = \phi/l_r$, where m_i denotes the mass of the i th BCP. Herein, we study block copolymer blends with large length ratios ($l_r > 10$). Based on our simulation results we propose that the co-assembly mechanism that induces morphological transitions in $(AB)_{hi}/(AC)_{lo}$ blends in selective solvents, requires the selective localization of short block copolymers at the interface and the corona of the assembled structures. This blending methodology has the potential to create nano-scale aggregates with multiple resolutions in a straightforward manner.

Methods

Computational Model

Dissipative Particle Dynamics (DPD)^{41,42} method was used to model diblock copolymer blends in solution. DPD is widely used in the modeling soft matter.^{43,46–50} We refer the reader to the Supporting Information (SI), for a detailed discussion of the model and simulation method.

The simulations adopt the standard DPD units⁴³ of length, $r_c = 1$, mass $m = 1$, energy $\varepsilon = k_B T = 1$, and time $\tau = 1$; as well as the friction coefficient of the dissipative force $\gamma = 4.5$. With a particle density $\rho_n = 3$ particles/ r_c^3 . For time integration we use a time step 0.04τ , to avoid thermal fluctuations larger than 1%. The evolution of the systems was performed during $1e10^6$ time steps. The simulations were conducted with the software LAMMPS,⁵¹ while the analysis and visualization of the computational results were performed with in-house codes and the software OVITO.^{52,53}

The computational results used cubic simulation boxes of size $L_{box} = 131r_c$, with periodic boundary conditions. Since the box size was approximately 12-fold the unperturbed radius of gyration, R_g^o , our results reflect aggregates with characteristic domain sizes commensurable in this box size. A detailed description of the box size definition is presented the in Supporting Information.

The dependency of the assembled morphologies with the process of preparation of the sample, is understood experimentally as a kinetic effect.^{3,10,54} Similarly, the initial density fluctuations in the simulation box affect the assembled structures. In these work we treat the kinetic effects induced by the initial polymer distribution in the system, such that we simulate different experimental polymer conditions that cannot be captured in the computable time spans of our simulations, due to the translational entropy penalty

In this paper we explored two different schemes of initial density fluctuations, these are: homo-

geneously dissolved and localized clusters of copolymers (See Supporting Information). These initial condition allowed us to obtain stable and metastable-assembled structures which have been verified experimentally for diblock copolymers blends in solution. We denote metastable aggregates the assemblies that depend on the initial polymer distribution. If those aggregates do not evolve within the time frame used in our simulations we consider them as metastable or kinetically trapped structures.

Diblock copolymer construction

The solvent was modeled as a sea of individual, interacting DPD particles. Diblock copolymers are coarse grained (or discretized) in sets of N interacting particles connected through spring potentials $u_{ij}^S = \frac{K_s}{2}(r_{ij} - r_o)^2$ with a spring constant $K_s = 50k_B T / r_c$ and equilibrium distance $r_o = 0.8r_c$. The $(AB)_{hi}$ molecules were modeled using a fixed number of particles, while the number of beads used in $(AC)_{lo}$ molecules was defined according to the length ratio l_r . We explore the influence of $(AC)_{lo}$ concentration over the assembled structures for a fixed $l_r = 15$, and different concentrations of $(AB)_{hi}$ (i.e., 1%, 8% and 17%). We associate these polymer concentrations with dilute (1%), dilute to semidilute transition (8%), and semidilute (17%) conditions. The amount of $(AC)_{lo}$ in this cases varies from 0 to 20%. The concentration of the copolymers were defined as the total number of particles per copolymer (i.e., $(AB)_{hi}$ and $(AC)_{lo}$) over the total number of particles in the system ($\rho_n L_{box}^3$).

In most of the DPD studies on diblock copolymers self-assembly reported in the literature^{16,25,26,31–33,37,55} $10 < N < 50$, however, in order to be able to reach large length ratio (i.e., $l_r \approx 15$, corresponding to blends of large and short diblock copolymers) we choose $N_{AB} = 192$ particles. We highlight that the study of such large l_r is cumbersome from the computational point of view since the computational model has to be able to capture the length scale of both BCPs. Furthermore, since the length scale of the aggregates is dominated by the large BCP, the box size needs to be large enough to capture the whole aggregate.

Characterization of self-assembled structures

Interfacial Area

The interfacial area between the A and B domains was measured following the methodology proposed by Stukowski,^{52,53} with a probe radius of $1.3r_c$. The interfacial area was approximated as the surface of the clusters formed by the A segments of the large molecular weight chains.

Gyration Tensor

We characterize the size and shape of the block copolymer chains in the system by computing the gyration tensor $\mathbf{R}$ of the coils, and each copolymer block. The gyration tensor can be written as

$$\mathbf{R} = \frac{1}{N} \sum_{i=0}^N \mathbf{r}_i \otimes \mathbf{r}_i, \quad (1)$$

where $\mathbf{r}_i$ is the coordinate of the i th particle with respect to the center of mass of the chain, and $\otimes$ denotes the dyadic product. Shape parameters derived from $\mathbf{R}$ are presented in SI.

Structure Factor

To compute the structure factor we divided our system in cubic bins of size r_{bin} , and calculated the local density of any specie i at each bin b (ρ'_{ib}). Hence, we computed the intensity of our structure factor as

$$I(k) = |S(\mathbf{k})|^2 = \frac{1}{B} \left| \sum_{b=1}^B \rho_{ib} \exp(-i\mathbf{k} \cdot \mathbf{b}) \right|^2, \quad (2)$$

where $\mathbf{k} = 2\pi\mathbf{l}/L_{box}$ is the wave vector, such that $\mathbf{l} = \{l_1, l_2, l_3\}$, and $-L_{box}/2 < l_i < L_{box}/2$.

Results and discussion

To investigate the effect of the addition of the $(AC)_{lo}$ chains ($l_r = 14.6$) over the assembled structures, we define four systems with different concentrations of $(AB)_{hi}$. In these systems, we vary

the ratio of ϕ $(AC)_{lo}$ to $(AB)_{hi}$ from 0 to 0.7. In order to clarify the importance of the B-C interactions (χ_{BC}), we conduct concentration experiments for athermal interactions $\chi_{BC} = \chi_{BB} = 0$. This condition can be associated with BCP blend of $(AB)_{hi} / (AB)_{lo}$.

Herein p_i is the fraction of each block in each $(AB)_{hi}$ or $(AC)_{lo}$ copolymer. We fixed the block at $A_{0.7}$ -b- $B_{0.3}$ and $A_{0.9}$ -b- $C_{0.1}$ (where the subscript indicates the block fraction p_i). Figure 1 illustrates the particle discretization applied. The asymmetry of the $(AB)_{hi}$ molecules in a solvent selective for B favors spherical and cylindrical aggregates. All simulations yield core-shell morphologies when $\phi = 0$ (single $(AB)_{hi}$ in solution). Under the current solvent-polymer interaction the coil size of the $(AC)_{lo}$ remains almost unchanged, and free chains of $(AC)_{lo}$ do not aggregate. We verify the evolution of the system to identify the equilibration of the aggregates. Supporting Figure 3, depicts the typical variation of the radius of gyration, R_g , for each of the A_{hi} and B_{hi} blocks. Snapshots of the simulations showing the stabilization of the structures are included.

Figure 1: Diblock copolymer representations in our dissipative particle dynamics simulations

Diluted and transition AB Concentrations

Naive simulations of polymer blends in the dilute regime do not exhibit phase separation in computable time spans due to the translational entropy penalty. Nevertheless, experimental evidence⁹

shows that assemblies can be formed at such concentrations. In order to overcome these transport penalties for the diluted condition, the segregation kinetics are modified by altering the initialization procedure of the chain positions. We adopt localized clusters (**LC**) of polymer. (For a detailed description of the initialization schemes see the Supporting Information)

The addition of $(AC)_{lo}$ induces morphological and topological transitions in poor and selective solvents. Figure 2 shows these transitions for solutions containing 8% of $(AB)_{hi}$. In poor solvents, complete polymer-solvent phase separation takes place, and the block copolymers create meso-scale segregated domains within the aggregates. Pure $(AB)_{hi}$ systems ($\phi = 0$) produce large lumps of B. As the amount of $(AC)_{lo}$ in the system increases the size of the B domains decreases and the segregation of the short $(AC)_{lo}$ chains to the interface acts as a compatibilizer for A and B, consequently the interfacial area increases.

Systems with a selective-solvent for B favor meso-phase separation in core-shell structures. The core-forming block is A given its large volume fraction, and lower affinity with the solvent. In general, when $\phi = 0$ the topology of the core and shell domains is simply connected (i.e., produces a single dense core), however spherical, cylindrical, and plate-like shapes might also result depending on the size of the micelles and the interfacial energy. When $\phi > 0$ meta-stable high-genus aggregates emerge. The genus characterizes the topology of an object,⁵⁶ indicating the number of holes or handles the object has. Thus, the spherical and plate-like micelles obtained at $\phi = 0$ have genus zero ($g = 0$), whereas for toroidal aggregates, $g = 1$. The difference in curvature between the short and long chains induces the topological transitions between different perforated aggregates. The localization of short diblock copolymers at the interface of the separated A-B domains reduces its bending energy, facilitating the formation of inner holes within the originally dense core-shell morphologies.

Kinetic and entropic factors stabilize the inner B domains in poor solvents and porous aggregates in selective solvents. In particular, systems with $\phi = 0$ evolve to zero-genus aggregates, irrespec-

Figure 2: Self-assembly of (AB)/(AC) copolymer blends in poor and selective solvents with 8% of $(AB)_{high}$, for different concentrations of $(AC)_{low}$. Solvent and the A blocks in $(AC)_{low}$ are omitted; beads of type C are presented in green. Blue domains correspond to the A block in $(AB)_{high}$, whereas red to B segments. Snapshots with the contour of the A blocks, in selective solvents are included as the bottom row to facilitate the visualization of the internal holes.

tive of the initial distribution of the polymer in the system. Conversely for systems with $\phi > 0$, meta-stable assemblies with $g \geq 0$ can be found when the starting copolymer distribution (initialization scheme) changes. Aggregates with different topology can then coexist in equilibrium. This is summarized in Figure 3. Remarkably, aggregates with $g \geq 0$ emerge independently of the B-C interactions (i.e., it happens for $(AB)_{hi} / (AC)_{lo}$ and $(AB)_{hi} / (AB)_{lo}$ blends). In non-equilibrium, kinetically trapped structures might dominate over the thermodynamically expected ones, however the effective surface tension to stabilize a hole must be low. Hence, the interfacial variation caused by the addition of short BCP chains favors the stabilization of the holes and inner domains.

Figure 3: Morphological transitions depending on the simulation starting condition (homogeneous copolymer distribution or in initial aggregates, indicated in squares); effect of addition of low molecular weight AC copolymers at large length ratios l_r

Perforated structures similar to those obtained in BCP blends have been reported in triblock copolymers in solutions.^{57–59} These structures are favored due to curvature minimization. In similar cases, the phase separation has been described by the Gibbs-Thomson equations,^{60,61} which include the interface curvature contribution to the free energy. In our simulations these perforated structures emerge as meta-stable trapped aggregates, due to the $(AC)_{lo}$ (or $(AB)_{lo}$) chains act as a compatibilizer and modify the curvature of the A-B interface

Semi-diluted AB systems

In semidilute systems (17% of $(AB)_{hi}$), we homogeneously solubilize the BCP at the beginning of the simulation (see starting conditions or initialization scheme **H** in SI). This would correspond to an experimental case, for which the BCP is first dissolved in a good solvent for A and B and by solvent exchange or temperature variation the solvent quality changes to poor for A and good for B. In this case, spherical micelles are the predominant equilibrium structures in solutions with pure AB, as Figure 4 shows. The blending process induces changes in the shape and size of the assemblies, as we depict in Figure 4 for blends containing $(AC)_{lo}$ and $(AB)_{lo}$.

Figure 4 presents the cross-section of assemblies simulated with length ratios $l_r = 14.6$. Additionally, to elucidate the role of the B-C interactions, Figure 4 includes morphological variations when $\chi_{BC} = 0$ (i.e., $(AB)_{hi} / (AB)_{lo}$ blends). The addition of the short $(AC)_{lo}$ chains modifies the curvature of the A-B interface and promotes large worm-like, and irregular micelles with reduced characteristic domain size, whereas the addition of short $(AB)_{lo}$ chains does not favor the growth of larger micelles.

Figure 5 gives a more quantitative information of the effect of blending smaller copolymer molecules on micellar size, given by the aggregation number Z , and the total number of micelles, M . For $(AB)_{hi} / (AC)_{lo}$ blends the number of micelles monotonically decreases as the weight fraction of the $(AC)_{lo}$ copolymer increases. When short copolymers with the neutral interaction ($(AB)_{lo}$) are added to the system the number of micelles decreases, but less than in the prior case. At the same time, while the size of micelles remains constant with addition of $(AB)_{lo}$, the addition of the $(AC)_{lo}$ copolymer induces an abrupt increase around $0.5 < \phi < 0.6$, where large aggregates, which are rather worm and network-like micelles are formed.

In addition to the micellar-size variation, we identify that the interfacial area increases with the

weight ratio (see Figure 3 in Supporting Information). The increment of the A-B interfacial area demonstrates the compatibilization effect of the short BCP chains, independently of the nature of B-C interactions (χ_{BC}). Nonetheless, the strength of χ_{BC} modifies the curvature of the aggregates, originating changes in the micellar size. These changes in curvature associated with hydrogen-bonding interactions could justify the domain size transition evidenced in the manufacture of nanoporous membranes, made of block copolymer blends.⁴⁰ Similarly, curvature transitions associated with large values of l_r and H-bonding interactions have been reported experimentally on melts of block copolymer mixtures.⁶²

Domain-size transition and anisotropy

We use the packing factor, p , to characterize the most probable morphology of the BCP aggregates in solution, based on geometrical considerations.² p is defined as $p = \bar{v}/a_0l$, where $\bar{v}$ is the molecular volume of the solvophobic block, a_0 is the interfacial area between A and B blocks, and l is the length of solvophobic block. Low p values favor spherical micelles, while increasing p values indicates deviations from spherical shapes. Bilayer morphology is reached when $p = 1$ (see Figure 1 in Supporting Information). The packing factor can be used to predict the morphology of block copolymers in solution by taking into consideration the volume of the coil, v , radius of gyration R_g (calculated from the gyration tensor, $\mathbf{R}$) and the end-to-end distance R_f (we refer the reader to SI for a detailed description of these parameters). For all conditions evaluated, we find $p \approx 0.4$ (see Supporting Figure 4) which is consistent with non-spherical micelles.² In the Supporting Information, Figure 6 compares the variation of the packing parameters (i.e., $\mathbf{R}$, R_f , p) for both A and B blocks as ϕ increases. We find that the deviation of B blocks from their unperturbed state is significantly larger than for A, and the addition of short BCPs reduces these deviations regardless χ_{BC} .

In systems containing pure $(AB)_{hi}$, due to the high interfacial energy (strong segregation) the conformation of both A and B is entropically penalized, and segments tend to be stretched away from their unperturbed condition. This stretching is substantially larger in the B blocks due to the

solvent interactions. The addition of the short $(AC)_{lo}$ (or $(AB)_{lo}$) chains compatibilizes the A and B domains, relaxing the entropic constraints that reduce the coil size of AB. We verify that the co-assembly mechanism in blends involves a strong contraction of the B domains. This mechanism is consistent with recent experimental evidence⁵⁴ suggesting that the dimension of the most soluble block governs the aggregation.

From the gyration tensor values, we corroborate that coils are predominantly prolate, and quantify the relative shape anisotropy, δ^* , between 0.38 and 0.4, regardless of ϕ . This interval is characteristic for theta and good-solvent conditions.⁶³

The addition of $(AC)_{lo}$ copolymers led to changes of the packing parameter independently of the character of χ_{BC} . In terms of the free energy change, we anticipate that only ϕ has an effect on G_{shell} and G_{core} contributions, independently of χ_{BC} . Thus, the morphological disparity between blends containing short chains $(AC)_{lo}$ or $(AB)_{lo}$ must be associated with variations of G_{intf} .

Morphological transition

Changes in the local conformation of the BCP coils cannot explain the evolution from spherical to elongated and irregular micelles observed at $\chi_{BC} < 0$ (see Figure (4)). We associate the co-assembly mechanism that dictates morphological transitions of the assemblies with the long-range distribution of the species in the system. Variations in the structure factor $S(\mathbf{k})$ of the core and shell-forming beads (A and B, respectively). Figure 6 shows the variation in $I(k) = |S(\mathbf{k})|^2$ with ϕ for neutral and strong B-C interactions. This variation demonstrates that the spatial distribution of the B segments within the shell is altered when the interaction with the short BCP is favorable, $\chi_{BC} < 0$. The main peaks of $I(k)$ are shifted to larger wave-vectors ($|\mathbf{k}|$) as ϕ increases, for $\chi_{BC} < 0$. In contrast, for neutral interactions there is a measurable shifting in the peaks when short copolymers are added, but this shift is independent of the amount of short BCP added. These results suggest that due to favorable B-C interactions, the short $(AC)_{lo}$ chains tend to segregate not only at

the A-B interface but also in the micelle coronas. Large amounts of $(AC)_{lo}$ between B segments explain the separation increase. In Figure 6, the curve for $\phi = 1.26$ exhibits a broader peak. This is associated to a critical condition, where the $(AC)_{lo}$ copolymer fully disturbs the order of the high molecular weight $(AB)_{hi}$ copolymers.

As a result of the selective localization of $(AC)_{lo}$ chains in the B-rich coronas, the curvature transitions associated with the interfacial free energy G_{intf} correlates with the variation in the effective AB-interfacial tension (γ). The magnitude of γ can be expressed as $\gamma = \gamma_{AB}\phi_{A1c}\phi_{Bs} + \gamma_{AS}\phi_{A1c}\phi_{Bs} + \gamma_{AC}\phi_{A1c}\phi_{Cs}$, where γ_{ij} denotes the interfacial tension between the species $i - j$, and $\phi_{i\alpha}$ represents the fraction of the i component in the α region (where c denotes core and s denotes shell). Typically, it is assumed that $\gamma_{ij} \propto \chi_{ij}^{1/2}$.⁶⁴ Figure 7 shows the fraction of short chains that is solubilized inside the micelles, $\bar{\zeta}_2 = \bar{W}_{AC}/W_{AC}$, where $\bar{W}_{AC}$ is the amount of short chains within the assemblies and W_{AC} is the total amount of $(AC)_{lo}$ in the system. We observe that $\bar{\zeta}_2$ is larger for $(AB)_{hi}/(AC)_{lo}$ blends. Furthermore, in these blends around 20% of the total $(AC)_{lo}$ chains are localized in the corona, whereas in $(AB)_{hi}/(AB)_{lo}$ mixtures this fraction is smaller than 10%. The increase of $\bar{\zeta}_2$ in the shell entails an increment in the amount of A segments in the B-rich corona. As a consequence, we can expect that due to the large swelling of the shell domain with shorter chains, γ is further decreased when $\chi_{BC} < 0$ condition, modifying the curvature of the aggregates.

Given the interfacial-energy difference between neutral and favorable B-C interactions, transitions in shape occur along with changes in the equilibrium size of the aggregates. Elongated and deformed micelles with lower interfacial tension favor the formation of larger aggregates with large aggregation numbers Z , due to the lower bending energy of the interface. Conversely, for neutral interactions spherical micelles with small Z remain nearly stable.

Remarkably, in Figure 7 we can observe that the fraction of short chains solubilized inside the micelles is nearly stable for a given χ_{BC} interaction. This result evidences the existence of a saturation condition (or equilibrium concentration between the phases). In this work we only focus on the effect of χ_{BC} compared to the athermal condition (AB_{hi}/AB_{lo}), and we do not explore further the effect of saturability for different strengths of the B-C interactions. However, our current results reveal that saturability effects of favorable interactions could be captured using the native DPD potentials. The study of these effects will be a matter of future work.

Conclusions

The meso-scale model of block copolymers (BCP) blends proposed in this paper, describes morphological transitions in the self-assembled structures induced by mixing block copolymers of different lengths. When the blended BCPs are highly dissimilar in size (large l_r), the low molecular weight chains (AC)_{lo} modulate the interfacial energy between the constitutive blocks of the larger molecules (AB)_{hi}. We describe the mechanisms that govern these shape transitions. First, short chains localize at the interface between the A and B blocks reducing the characteristic domain size of the aggregates. This mechanism depends only on the size and concentration of short chains. The second mechanism modifies the shape of the aggregates when B and C segments interact strongly. Hydrogen-bonding interactions induce segregation of the short BCPs into the B-rich corona. In order to increase the contacts between B and C blocks the aggregates evolve from spherical to worm-like micelles. The second mechanisms is absent in AB/AB blends, that is, when long and short chains are made of the same block copolymer.

Blending of block copolymers with large l_r appears as a straight forward approach to combine multiple resolutions in self-assembled domains. Due to the large difference in size the blend retains the characteristic packing properties of the large BCP, while the shape and topology of the aggregates is tuned by the concentration of short BCP.

In dilute polymer solutions, changes in the interfacial energy promote the assembly of a variety of metastable topologies. The presence of highly dissimilar chains facilitates the stabilization of different curvatures, such that perforated structures are produced. In pure AB-copolymer solutions, meta-stable micelles with different sizes and shapes are observed, however, these aggregates share the same topology (i.e., simply-connected core and shell). In contrast, BCP blend solutions exhibit a multiplicity of topologies as the concentration of short chains increases. Due to the possibility of creating perforated micelles with tunable porosity, we stress the potential of this blending methodology to design nanocarriers with many industrially relevant applications.

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Supporting Information Available

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Graphical TOC Entry

Figure 4: Morphological transitions for block copolymer blends in B-selective solvents with neutral and favorable B-C interactions, as the weight ratio of $(AC)_{lo}$ copolymer increases. Solvent and A block representations for the short BCP are omitted to facilitate the visualization; beads of type C are presented in green. Blue domains correspond to the A block in $(AB)_{hi}$, whereas red to B segments.

(a)

(b)

Figure 5: Effect of short chains concentration ϕ over the relative change in (a) the number of micelles M , and (b) the aggregation number Z .

Figure 6: Intensity of the structure factor of B segments for different weight ratios ϕ . Variations in the structure factor are presented for (a) $\chi_{BC} = 0$ ($(AB)_{lo} / (AB)_{hi}$) and $\chi_{BC} < 0$ ($(AC)_{lo} / (AB)_{hi}$) blends. Solid lines indicate the position of the main peaks for $\phi = 0$. The position of the main peaks after the addition of short BCPs is indicated. For $\chi_{BC} = 0$ the dashed lines shows the constant shifting at any $\phi = 0$.

Figure 7: Fraction of short chains solubilized within the micelles as a function of the concentration of total of added short chains. Dashed lines indicate chains solubilized in the core domains; solid lines corresponds to solubilization in the corona. We schematically show the variation in the amount of $(AC)_{Io}$ solubilized in the corona, and the interface. When B and C exhibit favorable interactions the concentration of short chains increases modifying the core-shell interfacial tension.