Morphology diagrams for $A_2B$ copolymer melts: real-space self-consistent field theory

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Abstract. Morphology diagrams for $A_2B$ copolymer melts are constructed using real-space self-consistent field theory (SCFT). In particular, the effect of architectural asymmetry on the morphology diagram is studied. It is shown that asymmetry in the lengths of $A$ arms in the $A_2B$ copolymer melts aids in the microphase separation. As a result, the disorder-order transition boundaries for the $A_2B$ copolymer melts are shown to shift downward in terms of $\chi N$, $\chi$ and $N$ being the Flory’s chi parameter and the total number of the Kuhn segments, respectively, in comparison with the $A_2B$ copolymers containing symmetric $A$ arms. Furthermore, perforated lamellar (PL) and a micelle-like (M) microphase segregated morphologies are found to compete with the classical morphologies namely, lamellar, cylinders, spheres and gyroid. The PL morphology is found to be stable for $A_2B$ copolymers containing asymmetric $A$ arms and M is found to be metastable for the parameter range explored in this work.

1. Introduction

Microphase separation in block copolymer melts[1, 2, 3, 4, 5, 6, 7] has motivated the scientific community over the last couple of decades. Delicate balance[3] of chain conformational entropy and repulsive interaction energy between unlike monomers allows block copolymers to readily self-assemble into a number of ordered morphologies. Typical morphologies[3, 8, 9] include lamellar, cylinder, sphere, gyroid and Fddd network phases, which have been proven to be equilibrium states.

Experimentally, the balance of the energy and entropy can be tuned by a number of molecular characteristics such as molecular weight[3], chain architecture[10, 11], conformational asymmetry[12, 13], polydispersity[14, 15, 16, 17, 18] and temperature. A number of studies[1, 2, 3, 4, 5, 6, 7] have been done to elucidate the effects of molecular weight, polydispersity, conformational asymmetry and temperature on the microphase separation in linear di-block copolymer melts. However, the effects of chain architecture are not that well established. On the computational side, this is primarily due to a large parameter space for the simulations and resulting large number of morphologies, which need to be compared in terms of their free-energy
to establish the morphology diagram. For the experiments, the challenge is to synthesize well-controlled macromolecules with non-linear architecture and reaching equilibrium by overcoming energy barriers.

In the 1970s, Fetters et al. [1] studied the morphologies and properties of star-block copolymers of polystyrene (PS) and polyisoprene (PI). Also in the 1970s, the synthesis of fairly well-defined multi-graft copolymers having polydiene backbones and PS side chains was reported [2, 4]. In the 1990s, systematic studies [19, 20, 21] aimed at elucidating the effect of branched architecture on the morphology and properties of block copolymers were initiated. Like the linear di-block copolymer melts, classical morphologies namely, lamellae, cylinders, spheres and gyroid, were observed in experiments [19, 20, 21] for the miktoarm star copolymers.

On the theoretical front, the morphological behavior of miktoarm star copolymers containing two kinds of blocks was described by Olvera de la Cruz [10] in the weak segregation limit and Milner [11] addressed the issue of microphase separation in the strong-segregation limit. The theory by Milner [11] accounts for the fact that the two kinds of blocks may differ in conformational characteristics, which results in a variation in the arms stretching at the junction point. Self-consistent field theory (SCFT) studies bridging the gap between the weak and strong segregation theories were done by Grason et al. [7, 22, 23]. Furthermore, dissipative particle dynamics (DPD) simulations [24] have been used to construct the morphology diagrams for $A_2B$ copolymer melts and reasonable agreement with the SCFT predictions [7, 23] has been established with the addition of new morphologies. Quite recently, a theory addressing the effects of polydispersity [25] on the microphase separation in $A_2B$ copolymers has been developed.

With the recent developments in the computational power and synthetic methodologies, synergetic studies on copolymers with non-linear architectures can be executed. Furthermore, theoretical studies in the weak and intermediate segregation limit can be performed. Motivated by these developments, we have studied the effects of chain architecture on the micro-phase separation in block copolymer melts and constructed morphology diagrams using the self-consistent field theory (SCFT).

In the present work, we have studied miktoarm star copolymer melts with a structure of $A_2B$ in which the total length and length of one of the $A$ arms is kept fixed while varying the fraction of $B$ block. Such a variation allows us to study architecturally asymmetric miktoarm copolymers (i.e., asymmetric $A$ arms) along with homopolymer and di-block copolymer melts. Morphology diagrams for architectural asymmetric miktoarm block copolymer melts are constructed using the real-space SCFT, without a prior knowledge about the morphologies. The study on the star copolymer melts is carried out in the weak and intermediate segregation limit.

This paper is organized as follows: details about the computational method (i.e., SCFT) are presented in section 2 followed by the results and conclusions in sections 3 and 4, respectively.

2. Computational method: SCFT

The SCFT is very well documented in the literature [26]. In the following, we only present the details relevant for this work. For the other details, we refer to an excellent review by Grason [7, 23].

Construction of the field theory starts from the particle description of the system in the form of a Hamiltonian having contributions from the chain stretching in Weiner form and short-range repulsive interaction energy in the Flory’s $\chi$ parameter form. Representing polymer chains as continuous curves, we write the partition function, $Z$ of the melts containing $n$ $A_2B$ chains as

$$Z = \frac{1}{n!} \int \prod_{\beta=1}^{n} D R_\beta(s) P [R_\beta(s)] \delta [\hat{\rho}_A(r) + \hat{\rho}_B(r) - 1] \exp \left[ -\chi \rho_0 \int dr \hat{\rho}_A(r) \hat{\rho}_B(r) \right]$$

(1)

where $P [R_\beta(s)]$ is the Weiner measure for the chain connectivity and $s$ is the contour variable specifying different locations on the curves $R_\beta$. Also, $\hat{\rho}_A(r)$ is the microscopic density of $A$.
defined as

$$\hat{\rho}_A(\mathbf{r}) = \frac{N}{\rho_0} \sum_{\beta=1}^{N_A} \int_0^1 ds \gamma_A(s) \delta[\mathbf{r} - \mathbf{R}_\beta(s)]$$

so that $N$ is the total number of the Kuhn segments along each chain and $\rho_0$ is the reference density ($1/l^3$, $l$ being the Kuhn segment length). Here, $\gamma_A(s)$ is a function, which is equal to 1 when $s$ lies along the $A$ blocks and 0 otherwise. A similar equation is written for $\hat{\rho}_B(\mathbf{r})$.

The chain architecture information is included in the path integral formulation written as Eq. 1. In order to switch from the particle description to the field theory, the Hubbard-Stratonovich transformation is used. In order to alleviate the complicated task of evaluating the functional integrals over the fields, these functional integrals are approximated by the value of the integrand at the optimum. This so called saddle-point approximation, leads to a set of non-linear equations, which need to be solved self-consistently using numerical methods. Furthermore, the free energy of the system at the saddle-point is readily accessible from these calculations, which, in turn, allow the construction of morphology diagrams for the co-polymer systems.

There are different ways of solving the non-linear set of equations obtained at the saddle-point. For the miktoarm copolymer melts, we have solved these set of equations in real-space starting from random guesses for the fields and densities. In particular, we have used the real-space algorithm presented in the work by Sides and Fredrickson[27], implemented in parallel. The real-space algorithm for the solution of the SCFT equations has the advantage that no a priori knowledge about the symmetry of morphologies is needed. This also means that the algorithm has the potential to discover new morphologies and give us the leverage to compare the free energies of different morphologies with each other, just by starting from different initial guesses.

In this work, we have focused on star co-polymers of the form $A_2B$, where the two $A$ arms can be of different lengths. For the construction of morphology diagrams, we have kept $N_{A1} + N_B = 100, N_{A2} = 25, N_j$ being the number of segments along the arm of $j$ type. Morphology diagrams are constructed by systematically varying the fraction of $B$ arm ($\phi_B = N_B/N$ where $N = N_{A1} + N_{A2} + N_B$) and $\chi$ parameter characterizing the repulsive interactions between the two components ($A$ and $B$). Also, we have taken the Kuhn segment lengths of different arms to be the same ($= l$) and ignored the effects of conformational asymmetry. We have done this on purpose to limit the parameter space and understand the effects of architectural asymmetry on the morphology diagrams.

Morphology diagrams were constructed by starting from random guesses for the equilibrium structures and searching for the minimum free energy state. Minimum free energy state is established by comparing the free energies of the final states obtained from different random guesses. Sometimes, the relaxation scheme used for solving the non-linear equations gets trapped in metastable or weakly unstable configurations. In order to remove topological defects and achieve global free energy minimum state, we have used a “zone annealing” technique in which a zone of reduced $\chi$ is moved across the simulation grid. Other details of the technique will be presented elsewhere. This procedure allows us to sort out the lowest free energy state of the system. All of the results presented below are obtained by solving the SCFT equations on a cubic grid containing 64$^3$ grid points with a grid spacing of $0.1$ (in units of $R_{go} = (N_{A1}/6)^{1/2}l$). For the special case of $\phi_B = 0.8$ with $N_{A2} = 25$ and $N_{A1} + N_B = 100, N_{A1} = 0$, (i.e., a linear di-block), we have used $R_{go} = (N_{A2}/6)^{1/2}l$ for making length dependent quantities dimensionless. Also, a time step of $0.01$ is used to solve the modified diffusion equations using the pseudo-spectral method[27].
3. Results and Discussions

In Fig. 1, we present the morphology diagrams for $A_2B$ star copolymer melts containing symmetric $A$ arms (Fig. 1(a)) and asymmetric $A$ arms (Fig. 1(b)). Both, the SCFT[22] and DPD[24] studies have already chalked out the morphology diagrams for $A_2B$ copolymers with symmetric $A$ arms. However, the SCFT study[22] has been carried out using spectral methods, where one has to presume the symmetry of morphologies. Furthermore, worm-like micelles are observed in the DPD simulations[24] in contrast to the sphere or cylindrical phase in the SCFT near the disorder-order transition around $\phi_B = 0.8$. Also, experiments by Pochan et al.[20] show the existence of microphase separated structures (micellar) without any underlying lattice.

Our real-space self-consistent field theory calculations for the $A_2B$ copolymers with symmetric arms (Fig. 1(a)) confirms the stability of classical morphologies such as lamellar, cylinders, spheres and gyroid in different parameter ranges. Just like linear di-block copolymers, in all of the curved morphologies, the minority component forms the interior and the majority components acts like a matrix. Fig. 1(a) is in excellent agreement with the spectral SCFT[22] study. However, Fig. 1(a) is in slight disagreement with DPD[24] study. The disagreement lies in the stability of perforated lamellar (PL) and worm-like micellar morphology as observed in the DPD study near $\phi_B = 0.5$ and $\phi_B = 0.8$, respectively. Our real-space SCFT calculations starting from random numbers as initial seeds for the fields and without the use of “zone annealing” technique show PL for $\phi_B = 0.5$. Furthermore, these calculations reveal the existence of microphase separated but not very well-ordered micellar structures (M) for $\phi_B = 0.8$. Isosurfaces of the density profiles of $A$ in the PL and M morphologies corresponding to $\phi_B = 0.5$ and $\phi_B = 0.8$, respectively, at $\chi N = 37.5$ are shown in Figs. 2(a) and 2(b), respectively. The M morphology has undulated cylinders and spheres coexisting with each other, without any underlying lattice. However, we have found that both the PL and M morphologies are metastable and the removal of defects using the “zone annealing” technique leads to more stable lamellar and cylindrical morphology, respectively, as shown in Fig. 1(a).

Fig. 1(b) shows the morphology diagram when we vary the volume fraction of $B$ block ($\phi_B$), while keeping volume fraction of one of the $A$ arms fixed at 0.2. The variation allows...
Figure 2. Isosurfaces of the density distributions of $A$ in the perforated lamellar (PL) morphology (a) and micelle-like (M) morphology (b).

us to put the morphologies of homopolymers, miktoarm copolymers with symmetric $A$ arms and linear di-blocks on the same diagram. For example, in Fig. 1(b), the leftmost column ($\phi_B = 0.2$) represents a miktoarm star copolymer with a very small $B$ arm. The rightmost column ($\phi_B = 0.8$) correspond to a linear di-block copolymer with $A$ as the minority component. Morphological transitions from the disordered to the spheres to the cylinders for $\phi_B = 0.8$ are in excellent agreement with other literature studies[6]. Furthermore, the morphologies for $\phi_B = 0.6$ are the same as for the miktoarm star co-polymers containing symmetric arms as shown in Fig. 1(a).

Comparing Figs. 1(a) and 1(b), it is clear that architectural asymmetry originating from distribution of segments among different $A$ arms has a significant effect on the morphology diagram. For example, we have found the PL morphology to be stable for miktoarm copolymers containing asymmetric $A$ arms in contrast to Fig. 1(a). Also, cylindrical morphology (with $B$ component forming the core) is found to be stable for $\chi N = 37.5, \phi_B = 0.5$, in qualitative agreement with Ref. [11]. Furthermore, comparison between the Figs. 1(a) and 1(b) reveals that the architectural asymmetry of $A$ arms plays a significant role in determining the disorder-order transition boundaries. For example, comparing the values of $\chi N$ at which an ordered morphology is first observed for $\phi_B = 0.8$ in Figs. 1(a) and 1(b), it is found that stronger repulsive interactions (i.e., higher $\chi N$ or lower temperature values due to the inverse dependence of $\chi$ on the temperature) are required for $A_2B$ to undergo microphase separation in comparison with the linear $AB$ diblock containing the same fraction of $B$. Note that linear di-block copolymer can be imagined as the $A_2B$ copolymer so that length of one of the $A$ arms is zero. By this argument, $A_2B$ copolymer in the form of a linear diblock has the highest asymmetry of $A$ arms. So, we can infer that architectural asymmetry originating from the length of $A$ arms helps in undergoing micro-phase separation. Comparing the $\chi N$ for the disorder-order transition from Figs. 1(a) and 1(b) for the same $\phi_B$’s, it is clear that this is true in general and we can conclude that architectural asymmetry aids in the microphase separation. This is consistent with the spectral SCFT studies[7].
4. Conclusions
For several decades there has been considerable attention focused on block copolymer materials, due largely to their ability to self-organize into a variety of morphologies having feature sizes on the scale of nanometers. It is known that block copolymers self-assemble into a rich range of three-dimensional nanoscale structures that can provide a suitable framework for the production of new and complex materials. In contrast to the case for simple linear block copolymers, the structure-morphology relationships for nonlinear block copolymers have yet to be thoroughly understood, a problem that has largely prevented their exploitation.

Our work has demonstrated that morphologies in $A_2B$ miktoarm star copolymer melts are sensitive to the architectural asymmetry. We have constructed the morphology diagrams for the $A_2B$ copolymer melts containing symmetric and asymmetric $A$ arms using the real-space self-consistent field theory without presuming the symmetry of ordered structures. In addition to the lamellar, cylinders, spheres and gyroids formed by the minority component, we have found the perforated lamellar (PL) morphology to be stable for $A_2B$ copolymers containing asymmetric $A$ arms. Also, we have found the PL and a micelle-like (M) morphology to be metastable for the $A_2B$ miktoarms with symmetric $A$ arms. This is in agreement with other literature studies carried out using spectral SCFT[22] and in disagreement with a DPD[24] study. Furthermore, comparison of the morphology diagrams for $A_2B$ copolymers containing symmetric and asymmetric arms reveal that architectural asymmetry of A arms aids the microphase separation. While this work was under review, we have come to know about recent work by Matsen[28] on $A_2B$ copolymers containing symmetric A arms. Our Fig. 1(a) is in agreement with Ref. [28]. Note that the PL morphology is found to be stable in Ref. [28] outside the parameter range explored in this work.

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