Symmetry breaking in particle-forming diblock polymer/homopolymer blends

Guo Kang Cheong^a, Frank S. Bates^a , and Kevin D. Dorfman^{a,1}

^aDepartment of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

Edited by Pablo G. Debenedetti, Princeton University, Princeton, NJ, and approved June 9, 2020 (received for review March 31, 2020)

Compositionally asymmetric diblock copolymers provide an attractive platform for understanding the emergence of tetragonally close-packed, Frank–Kasper phases in soft matter. Block-polymer phase behavior is governed by a straightforward competition between chain stretching and interfacial tension under the constraint of filling space at uniform density. Experiments have revealed that diblock copolymers with insufficient conformational asymmetry to form Frank–Kasper phases in the neat-melt state undergo an interconversion from body-centered cubic (bcc) close-packed micelles to a succession of Frank–Kasper phases (σ to C14 to C15) upon the addition of minority-block homopolymer in the dry-brush regime, accompanied by the expected transition from bcc to hexagonally packed cylinders in the wet-brush regime. Self-consistent field theory data presented here qualitatively reproduce the salient features of the experimental phase behavior. A particle-by-particle analysis of homopolymer partitioning furnishes a basis for understanding the symmetry breaking from the high-symmetry bcc phase to the lower-symmetry Frank–Kasper phases, wherein the reconfiguration of the system into polyhedra of increasing volume asymmetry delays the onset of macroscopic phase separation.

block polymer | Frank–Kasper phases | self-assembly | self-consistent field theory

Compositionally asymmetric AB diblock polymers form micelles with the minority A-block in the core to minimize enthalpically unfavorable A/B contacts. When a melt of these polymers is cooled below the order–disorder transition temperature, the micelles undergo a first-order phase transition and order on a lattice. Theory and experiments in the past four decades indicated that these particles form a body-centered cubic (bcc) phase (Fig. 1) throughout much of the sphere-forming region of the phase diagram (1, 2) with a small region of face-centered cubic (fcc) packing near the order–disorder transition (3, 4). The discovery of a Frank–Kasper σ phase (Fig. 1) in a diblock-copolymer melt in 2010 (5) upended the conventional wisdom that these materials only form close-packed structures. Typically found in metals and metallic alloys (6, 7), Frank–Kasper phases are tetragonally close-packed structures consisting of combinations of 12-sided, 14-sided, 15-sided, and 16-sided polyhedra. These building blocks can be arranged in a vast number of ways, with 27 known Frank–Kasper phases, and other packings proposed but not yet observed in nature (8). Since the original discovery of the σ phase in block-copolymer melts (5), three other Frank–Kasper phases have been identified: A15 (9–11), C14 (12–14), and C15 (12, 13). C14 and C15 are also known as Laves phases, a subset of Frank–Kasper phases consisting of only Z12 and Z16 polyhedra (Fig. 1). Frank–Kasper phases are periodic approximants to quasicrystals, and a dodecagonal quasicrystal, associated with the σ phase, has been observed as well in diblock-copolymer melts (15). In addition to block polymers, Frank–Kasper phases and quasicrystals have been reported in a wide range of other soft materials, including dendrimers (16, 17), liquid crystals (18–22), and shape amphiphiles (23, 24), including a notable discovery of the Z-phase in the latter (25). With the existence of Frank–Kasper phases in soft matter now

firmly established, the challenge has moved toward understanding the factors giving rise to these low-symmetry phases over high-symmetry, close-packed structures like bcc.

In the context of neat linear diblock-copolymer melts, there now exists evidence supporting three independent factors giving rise to Frank–Kasper phases. First, these phases only emerge for conformationally asymmetric block polymers, where the block comprising the matrix is stiffer (i.e., characterized by a smaller volume-normalized statistical segment length) than the core block (9, 26–29). For such systems, the borders of the Voronoi cells are imprinted on the core–matrix interface. The interfacial and corona distortion alters the delicate balance of interfacial tension and chain stretching that otherwise favors close-packed spheres when the matrix is soft and selects packings with higher sphericity (30). Second, owing to the nearly degenerate free energies of different Frank–Kasper phases in diblock polymers (12, 29), thermal processing can access different ordered states (12, 13), with the C14 and C15 Laves phases being accessible to date in the neat-melt state only by thermal processing. Third, there is evidence that lower molecular-weight systems, which increase the self-concentration of the chains, also stabilize Frank–Kasper phases (31). However, the appearance of Frank–Kasper phases within the context of self-consistent field theory (SCFT) calculations (12, 27, 29), which are only strictly valid as the degree of polymerization $N \rightarrow \infty$, indicates that high self-concentration is not a necessary condition for Frank–Kasper phase formation.

While further increasing conformational asymmetry and exploiting different processing paths are feasible approaches to

Significance

Frank–Kasper phases are low-symmetry packings of particles, originally discovered in metals and alloys and now observed in a wide range of soft matter. Understanding how such low-symmetry phases arise in soft materials is an outstanding challenge, as they tend to form high-symmetry, close-packed structures. This work uncovers a mechanism for generating Frank–Kasper phases in diblock copolymers with soft matrices that prefer to form a body-centered cubic structure in the neat-melt state. As homopolymer is loaded into the core of the particles, the system selects a series of Frank–Kasper phases with increasing particle volume asymmetry until eventually the homopolymer phase separates from the block polymer.

Author contributions: G.K.C., F.S.B., and K.D.D. designed research; G.K.C. performed research; G.K.C. and K.D.D. analyzed data; G.K.C. and K.D.D. prepared the manuscript; and G.K.C., F.S.B., and K.D.D. edited versions of the manuscript.

The authors declare no competing interest.

This article is a PNAS Direct Submission.

Published under the [PNAS license](#).

Data deposition: The input and output files have been deposited in the Data Repository at the University of Minnesota (<https://doi.org/10.13020/xfwb-9k72>).

See [online](#) for related content such as Commentaries.

¹To whom correspondence may be addressed. Email: dorfman@umn.edu.

This article contains supporting information online at <https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2006079117/-DCSupplemental>.

First published July 7, 2020.

Fig. 1. Illustration of the unit cells for a bcc phase, the Frank-Kasper σ phase, and the C14 and C15 Laves phases. Particle colors correspond to Z8 (black), Z12 (red), Z14 (blue), Z15 (green), and Z16 (yellow). Illustrative polyhedra are included for each particle type.

widen the range of diblock-copolymer compositions and temperatures that produce Frank-Kasper phases, blending provides considerably more versatility within a relatively straightforward experimental platform. For example, experiments performed with blends of lamellar-forming diblock polymer and a disorder-forming diblock polymer furnished two Frank-Kasper phases, σ and A15, and a dodecagonal quasicrystal (32). Related SCFT calculations (13, 33, 34) reveal that blending two diblock copolymers with different molecular weights and volume fractions of the minority block can substantially increase the region of the phase space where Frank-Kasper phases are stable. In the blended system, the two different block copolymers tend to reside at different locations within the particles (33) to minimize the chain-stretching penalty for reaching the edges of the Voronoi cells.

Blending a diblock copolymer with a homopolymer also leads to the emergence of Frank-Kasper phases. Experiments have probed the addition of homopolymer that is similar to the molecular weight of either the matrix block (35) or the core block (36). In the former case, the addition of the matrix homopolymer led to the formation of a σ phase. In the latter case, the system underwent a sequence of transitions from bcc to σ to C14 to C15 with the addition of core homopolymer in the dry-brush regime (37), i.e., when the core homopolymer is of similar length to the core block (36). Reducing the molecular weight of the homopolymer loaded into the cores of the micelles shifted the system into a wet-brush regime, wherein the only ordered states observed were bcc and hexagonally packed (hex) cylinders (36). These experiments (36) used a diblock copolymer that produced only a bcc phase in the neat-melt state (31), indicating that high conformational asymmetry is not a prerequisite for Frank-Kasper phase formation during blending with a homopolymer.

SCFT provides an ideal platform for understanding the symmetry breaking in blends of AB diblock polymers with A-homopolymers by facile discrimination of the placement of A-block and A-homopolymer chains within the domains. Zhao and Li (38) used SCFT to examine the phase behavior of AB₄ miktoarm polymers under the addition of A-homopolymer, where the homopolymer is at least as long as the A-block and thus deep into the dry-brush regime (37). In a neat melt, the high conformational asymmetry of an AB₄ miktoarm polymer exhibits

a sequence of fcc to bcc to σ to A15 (38), corresponding to an increasing average isoperimetric quotient and consistent with the arguments of sphericity (30). Addition of A-homopolymer leads to the emergence of both C14 and C15 Laves phases, accompanied by changes in the volume asymmetry of the particles, the various contributions to the free energy, and the distributions of the different components within the domains (38). In the present contribution, we build on these initial observations (38) to provide a deeper understanding of the emergence of different Frank-Kasper phases in experiments on diblock polymer/homopolymer blends (36).

Results

We have performed SCFT calculations for a system that mimics the experiments of Mueller et al. (36) on poly(styrene-*b*-1,4-butadiene) block polymers blended with poly(1,4-butadiene) homopolymer. The minority A-block in their experiments is poly(1,4-butadiene), with a volume fraction $f_A = 0.18$. The ratio of statistical segment lengths $b_A/b_B = 1.31$, where b_i is the statistical segment length of block i (31). The corresponding conformational asymmetry of $\epsilon \equiv (b_A/b_B)^2 = 1.7$ is insufficient to form a Frank-Kasper phase in SCFT (27) or in experiments on the neat diblock-polymer melt (31). The experimental system is thus significantly different from the AB₄ miktoarm/A-homopolymer system examined previously by SCFT (38), as both theory (26, 27, 38) and experiments (9) indicate Frank-Kasper phases form in neat melts of miktoarm copolymers because the branches in the matrix impart a very high degree of conformational asymmetry.

We examine here the phase behavior of this system at the fixed value of $\chi N = 25$, where χ is the Flory-Huggins parameter, and N is the degree of polymerization of the diblock polymer, for different values of the volume fraction of the block polymer, ϕ_1 , down to $\phi_1 = 0.70$. At $\chi N = 25$, SCFT predicts that the neat diblock-copolymer melt is fcc. The fcc-bcc two-phase window only occupies less than 1% of the phase diagram and is immediately overtaken by bcc at higher values of ϕ_1 . As expected (3), increasing to $\chi N = 30$ (SI Appendix, Fig. S1A) produces a bcc state in the neat melt and lowering to $\chi N = 20$ (SI Appendix, Fig. S2B) produces a disordered melt.

Fig. 2 furnishes phase diagrams for three different degrees of polymerization N_H of the homopolymer, where $\alpha = N_H/f_A N$ represents the ratio of the degree of polymerization of the A-homopolymer to the A-block (36). For $\alpha = 1$, the system is in the dry-brush limit, where penetration of the homopolymer into the space occupied by the associated block is limited. Past the narrow window of fcc stability, the phase sequence of bcc to σ to C14 to C15 qualitatively agrees with experiments obtained at $\alpha = 1.08$ (36), with the caveat that the experimental sequence of phases was obtained by simultaneously decreasing ϕ_1 and increasing temperature, which may be related to the fluctuation-induced stabilization of Frank-Kasper phases (9) that is neglected in SCFT. Eventually, SCFT predicts that the system macroscopically phase separates into C15 and a disordered homopolymer-rich phase, consistent with experiments (36) on this system and SCFT results obtained for AB₄ miktoarm polymers (38). While canonical ensemble calculations produce a C14 phase within the two-phase window, the concomitant grand-canonical ensemble calculations reveal that the C14/homopolymer and C15/homopolymer tie lines are indistinguishable. We thus posit that the equilibrium two-phase system is C15/homopolymer but caution that the free-energy differences between these two possibilities are small (SI Appendix, Tables S1–S3). Additional calculations at $\chi N = 20$ (SI Appendix, Fig. S2B) show a similar sequence of phases but with a disordered neat melt and fcc as the classic sphere-forming phase rather than bcc, and $\chi N = 30$ (SI Appendix, Fig. S1) produces only bcc followed by the Frank-Kasper phase sequence.

Fig. 2. SCFT phase diagram for blending of an AB diblock polymer with A-homopolymer for different ratios $\alpha = N_H/f_A N$ of the degree of polymerization of the A-homopolymer to the A-block and volume fractions ϕ_1 of the diblock copolymer: $\alpha = 1$ (A), $\alpha = 7/9$ (B), and $\alpha = 2/3$ (C). The symbols indicate state points for SCFT calculations in the canonical ensemble. Phase boundaries between these state points were obtained by grand-canonical ensemble calculations. Symbols correspond to fcc (gray open diamond), bcc (dark purple filled square), σ (light purple open circle), C14 (green filled circle), C15 (blue open triangle), and hex cylinders (red filled triangle) obtained from canonical ensemble calculations. A15 was also a candidate phase, but no regions of A15 stability were observed. Two-phase regions between ordered states are indicated by light shading; in many cases, these regions are too narrow to be depicted. The hashed areas indicate two-phase regions that correspond to equilibrium between an ordered phase and a disordered phase.

Likewise, calculations at $\chi N = 25$ for the conformationally symmetric case $\epsilon = 1$ (SI Appendix, Fig. S3B) produce bcc followed by the same progression of Frank–Kasper phases upon addition of homopolymer, indicating that conformational asymmetry is not a necessary condition. Moreover, the neat diblock melt for $\epsilon = 1$ produces bcc, indicating that conformational asymmetry is required to produce the fcc phase in Fig. 2 and SI Appendix Figs. S1A and S2B.

As the homopolymer molecular weight decreases to $\alpha = 7/9$, Fig. 2B indicates a loss of the C14 and C15 phase and the emergence of a hex cylinder phase over a large range of ϕ_1 that we examined. Continued reduction of the degree of polymerization of the homopolymer to $\alpha = 2/3$ in Fig. 2C leads to further extinction of the Frank–Kasper phase. This phenomenon is consistent with experiments at $\alpha = 0.6$ and has been attributed to a transition from dry- to wet-brush behavior (36). Qualitatively similar behavior occurs at a lower $\chi N = 20$ (SI Appendix, Fig. S2B). When $\epsilon = 1$ and $\chi N = 25$ (SI Appendix, Fig. S3B), the extinction of Frank–Kasper phases with decreasing α is even more pronounced, consistent with the ability of conformational asymmetry to stabilize Frank–Kasper phases (27).

Overall, the SCFT calculations capture the salient aspects of the experimental phase behavior, namely the sequence of the Frank–Kasper phases as the volume fraction of homopolymer increases and the transition from Frank–Kasper particle phases to a cylindrical phase as the homopolymer degree of polymerization decreases. SCFT does not provide a quantitative prediction of the stability windows for Frank–Kasper phases due to their nearly degenerate free energies (SI Appendix, Tables S1–S10), consistent with prior work (9, 12, 13, 27, 39, 40).

To investigate further the transition between wet- and dry-brush regimes, Fig. 3 examines the volume fractions ϕ_A and ϕ_H of the A-block and homopolymer repeat units, respectively, along the [111] direction of the bcc phase, which is the simplest case to analyze, at a block-polymer volume fraction of $\phi_1 = 0.97$. As the homopolymer degree of polymerization N_H increases, Fig. 3A indicates that the cores of the micelles swell slightly, using $\phi_A + \phi_H = 0.5$ as a reasonable cutoff for the A-rich region of the micelle. While the swelling effect is small, the increase in the apparent degree of segregation is more significant. The origin of the increased segregation is a dewetting of the A/B interface of

the micelles as N_H increases, with Fig. 3B demonstrating a significant increase in the homopolymer segregation toward the core of the micelle (37). The observation of increased wetting of the brush with decreasing homopolymer molecular weight, and the eventual formation of a cylindrical phase in Fig. 2 for the shorter homopolymers, is consistent with the wet-brush model proposed by Mueller et al. (36) and thus consistent with their rationale for the emergence of a hex cylinder phase. Similar results are

Fig. 3. Illustration of the transition from the dry-brush to wet-brush regimes as the homopolymer molecular weight decreases at $\chi N = 25$. (A) Volume fraction of the A-blocks in the bcc phase at $\phi_1 = 0.97$ along the [111] direction for $\alpha = 1$ (red squares), $\alpha = 7/9$ (black circles), and $\alpha = 2/3$ (green triangles), where the position is made dimensionless with $\sqrt{3}a$ for the unit-cell parameter a . (B) Ratio of the A-homopolymer to A-block volume fractions for the conditions in A.

Table 1. Total volume fraction of the A-monomers, $\phi_A + \phi_H$, at the center of the micelles (i.e., the Wyckoff positions) for the dry-brush case $\alpha = 1$ and $\chi N = 25$

Phase	ϕ_1	Wyckoff Position	Polyhedron	$\phi_A + \phi_H$
bcc	0.97	—	Z8	0.980
σ	0.94	2b	Z12	0.988
		4f	Z15	0.992
		8i	Z12	0.988
		8i'	Z14	0.991
		8j	Z14	0.991
C14	0.92	2a	Z12	0.993
		4f	Z16	0.997
		6h	Z12	0.993
C15	0.85	8a	Z16	0.999
		16d	Z12	0.999

Results correspond to canonical ensemble SCFT calculations appearing in Fig. 2. The bcc phase has one particle type, so it does not have a Wyckoff position.

obtained at $\chi N = 20$ (SI Appendix, Fig. S24) and for $\epsilon = 1$ at $\chi N = 25$ (SI Appendix, Fig. S34).

The apparent increase in segregation strength in the dry-brush regime observed in Fig. 3 for bcc is maintained for the Frank–Kasper phases. Indeed, Table 1 shows that the ejection of the B-block from the particle core is even stronger for the Frank–Kasper phases, with an increase from a total A volume fraction 0.980 for bcc to up to 0.999 for the Z16 particles in C15. The particle centers are defined by their Wyckoff positions, which are unaffected by the addition of homopolymer (SI Appendix, Figs. S4 and S5). Similar to what was observed in Fig. 3 for bcc, the purity of the A-polymers at the center of the particles is driven by partitioning of the homopolymers to the particle core and the A-block toward the perimeter of the particle core. Owing to the distorted shapes of the polyhedra in Frank–Kasper phases (30), it is not straightforward to analyze the homopolymer and block-polymer volume fractions in a manner akin to what we did for bcc in Fig. 3. Fig. 4 provides an alternate approach by examining the volume distribution for the σ phase in the (001) plane, which slices through four of the five different particle types in the σ phase. The trend is analogous to what was observed for bcc, with significant partitioning of the homopolymer to the interior of the particles.

Fig. 4 suggests that the effect of the partitioning of homopolymer to the particle center is stronger for a Frank–Kasper phase than for bcc. To investigate this point further, Fig. 5 compares the relative volume fraction of the homopolymer at the center of each particle in the dry-brush limit to the total volume fraction of A-polymers. Similar results are obtained at other conditions (SI Appendix, Figs. S1B, S2C, and S3C). Overall, Frank–Kasper phases exhibit an increase in the homopolymer volume fraction at the particle center of approximately 50% when compared to bcc. Interestingly, the homopolymer volume fraction for a given phase is a monotonically increasing function of the coordination number of the number of faces in the polyhedra, which are themselves increasing in volume with increasing coordination number (30, 38). Similarly, the 12-sided polyhedra contain a higher volume fraction of homopolymer in the centers of the particles in the Laves C14 and C15 phases than the Frank–Kasper σ phase, which arises in part due to the increased homopolymer volume fraction when the Laves phases are stable and is consistent with the larger volume asymmetry among different particles in the Laves phases (12).

To understand the relative partitioning of the homopolymer between different types of particles within a single phase, Fig. 6 tracks the evolution of the homopolymer volume fraction at the centers of the C15 particles in its relatively wide stability

region for $\alpha = 1$, which clearly illustrates the basic phenomena. At the onset of the stability window, the larger Z16 particle has approximately 17% higher volume fraction of homopolymer than the smaller Z12 particle, indicating a preferential loading of the larger particle first. As the homopolymer volume fraction increases, the relative differences in homopolymer volume fraction at the particle centers decrease to approximately 5%. Similar results are obtained at other conditions (SI Appendix, Figs. S1C, S2D, and S3D).

Discussion

The key issue posed by our SCFT calculations and the related experiments by Mueller et al. (36) is understanding the origin of the transition from bcc to σ to C14 to C15 upon the addition of homopolymer to the cores of the micelles in the dry-brush limit. Explanations proposed for the formation of Frank–Kasper phase in other diblock-copolymer systems are unlikely to be applicable to the present case. The conformational-asymmetry mechanism (27), which has been particularly powerful in explaining the formation of Frank–Kasper phases in neat diblock-copolymer melts (5, 9, 12), cannot provide a mechanism for their formation in this blended system; the stiffness of the matrix chains is imposed by the corona block chemistry and is unaffected by additives to the micelle cores. The addition of homopolymer does swell the micelle core (38), and it is tempting to propose that the swelling leads to compression of the matrix chains, which then imprints the shape of the polyhedra more strongly on the A/B interface. However, the system can relieve any such compression by expanding the unit-cell size, which is indeed the case in our calculations (SI Appendix, Figs. S6 and S7). Likewise, the basis for the enhanced stability of Frank–Kasper phases in blends of two diblock copolymers (13, 33, 34), which relies on the different block polymers partitioning within the particles to relieve chain stretching, cannot be the stabilizing mechanism in the presence of homopolymer, which simply partitions into the core and pushes the A-block toward the perimeter.

We thus seek an alternate mechanism for stabilization of Frank–Kasper phases upon the addition of homopolymer to micelles where the core and matrix blocks are of similar stiffness, i.e., for low conformational asymmetry. We posit that the increasing volume asymmetry of the particles in the different

Fig. 4. Volume fraction distribution in the (001) plane for the σ phase for the dry-brush case $\alpha = 1$ and block-polymer volume fraction $\phi_1 = 0.94$ at $\chi N = 25$. The 2b particle is on the corners, four of the 8i particles are proximate to the edges of the unit cell, two 4f particles are near the center, and four 8i' particles comprise the remainder of the particles in the image. Note that the (001) plane slices these particles at different distances from their centers and that the A/B interfaces of the particles themselves are asymmetric. The A-rich regions of the 8j particles do not intersect this plane. The transition between colors is selected to highlight different components in different locations.

Fig. 5. Volume fraction of the homopolymer, ϕ_H , relative to the total volume fraction of A-monomers at the center of a micellar particle, $\phi_A + \phi_H$, for the dry-brush case $\alpha = 1$ at $\chi N = 25$. Results correspond to canonical ensemble SCFT calculations appearing in Fig. 2. The notation refers to the Wyckoff positions of the particles and the number of faces in the polyhedra. Insets show the planar graph forms of each of the polyhedra.

particle-forming phases explains the order of their progression. The preferred ordered particle-forming state at the conformational asymmetry $\epsilon = 1.7$ and $\chi N = 25$ is fcc. Now consider what happens upon the addition of a small amount of homopolymer. If one cannot resolve the homopolymer from the core block, the data in Fig. 3 would lead one to interpret the system as a higher degree of segregation, or, equivalently, a higher χN . This effect produces the bcc phase, which is the preferred packing for a neat melt with low conformational asymmetry (27) but at a higher χN (*SI Appendix*, Fig. S14). As additional homopolymer is added and partitions toward the core of the bcc particle, it eventually reaches a solubility limit. At this point, the system is confronted with two options: macroscopic phase separation or an order–order transition to a Frank–Kasper phase. The system selects a transition to the σ phase. The selection of σ is, at first glance, analogous to its selection by conformationally asymmetric diblock polymers as χN increases (27). However, the symmetry-breaking mechanism differs for the blended system. While the morphology of the σ phase is dramatically different from bcc, it has the least particle volume asymmetry among the Frank–Kasper phases observed here (38), with the relative volumes all lying between 91.0 and 106.5% of the mean (30). Fig. 5 further indicates a relative partitioning of the homopolymer into the higher coordination number 4f particle, which is also the largest particle (30). We did not observe a stable region of A15, which is consistent with our argument; the two particles in A15 are of lower coordination number (Z12 and Z14) and very similar in relative volume (100.8 and 97.7%) (38). We posit that this soft matrix prefers bcc and will only transition to a Frank–Kasper phase that offers sufficient volume asymmetry to accommodate the additional homopolymer. Once the particles in σ are saturated with homopolymer, the system selects the next highest volume asymmetry (C14; relative volumes between 113.9 and 92.8%) (38) and the process repeats again to yield C15 (relative volumes of 114.2 and 92.2%) (38). At this point, there is no known Frank–Kasper phase in block polymers with a higher volume asymmetry. Under the addition of even more homopolymer in the dry-brush limit, the system is then forced to undergo macroscopic phase separation. This partitioning mechanism is robust with respect to χN (*SI Appendix*, Figs. S1B and S2C) and conformational symmetry (*SI Appendix*, Fig. S3C).

The SCFT results obtained here for a system with relatively low conformational asymmetry, as well as for no conformational asymmetry (*SI Appendix*, Fig. S3), differ from previous SCFT results obtained for AB₄ miktoarm polymers (38), which have exceptionally high conformational asymmetry. For example, the phase sequence for $\alpha = 1$ and $f_A = 0.2$ exhibits a transition from fcc to σ to C14, without a C15 regime. Similar results for $f_A = 0.28$ yield σ as the equilibrium phase for the neat melt, with a transition to C15, while $f_A = 0.32$ produces A15 in the neat melt and transitions to hex cylinders with added homopolymer. If the homopolymer length increases further to a ratio of $\alpha = 1.25$, the AB₄ miktoarm system now exhibits a transition from A15 to σ to C15, followed by phase separation. The particular Frank–Kasper phases for the neat polymer melts that emerge in the AB₄ miktoarm system arise from the conformational-asymmetry argument (27). Nevertheless, even for this different system, Frank–Kasper phases of increasingly higher volume asymmetry are selected as the homopolymer volume fraction increases, consistent with our result.

Our analysis benefits from the ability of SCFT to readily distinguish between the homopolymer and minority-block within the particle cores, since these are distinct entities in the calculation (41). An outstanding question related to the volume-asymmetry mechanism is whether the selective partitioning of the homopolymers to the larger particles can be observed experimentally. There is a body of prior work on combining small-angle X-ray scattering and small-angle neutron scattering to identify the locations of homopolymers in block-polymer microstructures (42, 43), and microscopy has also been employed for this purpose (44). The small domain sizes of the particles in these phases and the subtle (but important) differences in A-polymer volume fractions within different particles pose nontrivial experimental obstacles, but it may be possible to observe the partitioning effect through changes in the relative intensity of the scattering from the Z16 particles in C15 relative to the Z12 particles as the homopolymer volume fraction increases. Such an experimental confirmation would firmly establish volume asymmetry as one of the growing number of mechanisms (12, 27, 30) giving rise to Frank–Kasper phases in block polymers.

It remains to be seen whether this volume-asymmetry mechanism holds for other soft matter, where forming a dry-brush regime is no longer possible. For example, C14 and C15 Laves phases have been observed to emerge from a bcc phase in lyotropic liquid crystals (22) by fixing the loading of oil within the micelle core and decreasing the head-group hydration number. The oils used in surfactant experiments are low molecular-weight molecules and might be assumed to form a wet brush with the hydrocarbon portion of the surfactant molecules. However, the qualitative rules associated with the transition from wet-brush ($\alpha \approx 1/2$) to dry-brush ($\alpha \approx 1$) behavior when homopolymer is

Fig. 6. Volume fraction of the homopolymer, ϕ_H , relative to the total volume fraction of A-monomers at the center of the micellar particle, $\phi_A + \phi_H$, for C15 for $\alpha = 1$ and $\chi N = 25$ due to the addition of homopolymer. The color coding corresponds to Fig. 5.

mixed with block polymer do not translate directly to the case of surfactant and oil, which are characterized by the extreme limit of self-concentration (31). Analogous experiments with a fixed hydration number but varying the oil loading would provide an ideal test for the generality of the volume-asymmetry mechanism.

Materials and Methods

Self-consistent field calculations were performed using the open-source Polymer Self Consistent Field software package (41) with combined unit-cell

and field relaxation (45), using canonical ensemble calculations followed by grand-canonical ensemble calculations to locate the phase boundaries and two-phase regions (46). Additional details of the SCFT calculations are provided in *SI Appendix, Supplemental Information Text*. The input and output files have been deposited in the University Digital Conservancy at the University of Minnesota at <https://doi.org/10.13020/xfwb-9k72>.

ACKNOWLEDGMENTS. We acknowledge discussions with Prof. Mahesh K. Mahanthappa, Aashish Jayaraman, and Andreas J. Mueller. This work was supported by the NSF Grant DMR-1719692. Computational resources were provided, in part, by the Minnesota Supercomputing Institute.

1. L. Leibler, Theory of microphase separation in block copolymers. *Macromolecules* **13**, 1602–1617 (1980).
2. A. K. Khandpur *et al.*, Polyisoprene-polystyrene diblock copolymer phase diagram near the order-disorder transition. *Macromolecules* **28**, 8796–8806 (1995).
3. M. W. Matsen, F. S. Bates, Unifying weak- and strong-segregation block copolymer theories. *Macromolecules* **29**, 1091–1098 (1996).
4. E. W. Cochran, C. J. Garcia-Cervera, G. H. Fredrickson, Stability of the gyroid phase in diblock copolymers at strong segregation. *Macromolecules* **39**, 2449–2451 (2006).
5. S. Lee, M. J. Bluemle, F. S. Bates, Discovery of a Frank-Kasper σ phase in sphere-forming diblock copolymer melts. *Science* **330**, 349–353 (2010).
6. F. C. Frank, J. S. Kasper, Complex alloy structures regarded as sphere packings. I. Definitions and basic principles. *Acta Crystallogr.* **11**, 184–190 (1958).
7. F. C. Frank, J. S. Kasper, Complex alloy structures regarded as sphere packings. II. Analysis and classification of representative structures. *Acta Crystallogr.* **12**, 483–499 (1959).
8. M. Doutour Sikić, O. Delgado-Friedrichs, M. Deza, Space fullerenes: A computer search for new Frank-Kasper structures. *Acta Crystallogr. A* **66**, 602–615 (2010).
9. M. W. Bates *et al.*, Stability of the A15 phase in diblock copolymer melts. *Proc. Natl. Acad. Sci. U.S.A.* **116**, 13194–13199 (2019).
10. M. W. Bates *et al.*, Synthesis and self-assembly of AB_n miktoarm star polymers. *ACS Macro Lett.* **9**, 396–403 (2020).
11. K. K. Lachmayr, C. M. Wentz, L. R. Sita, An exceptionally stable and scalable sugar-polyolefin Frank-Kasper A15 phase. *Angew. Chem. Int. Ed.* **59**, 1521–1526 (2020).
12. K. Kim *et al.*, Thermal processing of diblock copolymer melts mimics metallurgy. *Science* **356**, 520–523 (2017).
13. K. Kim *et al.*, Origins of low-symmetry phases in asymmetric diblock copolymer melts. *Proc. Natl. Acad. Sci. U.S.A.* **115**, 847–854 (2018).
14. S. Jeon *et al.*, Frank-Kasper phases identified in PDMS-*b*-PTFEA copolymers with high conformational asymmetry. *Macromol. Rapid Commun.* **40**, 1900259 (2019).
15. T. M. Gillard, S. Lee, F. S. Bates, Dodecagonal quasicrystalline order in a diblock copolymer melt. *Proc. Natl. Acad. Sci. U.S.A.* **113**, 5167–5172 (2016).
16. G. Ungar, Y. Liu, X. Zeng, V. Percec, W. D. Cho, Giant supramolecular liquid crystal lattice. *Science* **299**, 1208–1211 (2003).
17. X. Zeng *et al.*, Supramolecular dendritic liquid quasicrystals. *Nature* **428**, 157–160 (2004).
18. R. Vargas, P. Mariani, A. Gulik, V. Luzzati, Cubic phases of lipid-containing systems: The structure of phase Q²²³ (space group Pm3n). An X-ray scattering study. *J. Mol. Biol.* **225**, 137–1345 (1992).
19. J. M. Seddon, N. Zeb, R. H. Templer, R. N. McElhaney, D. A. Mannock, An Fd3m lyotropic cubic phase in a binary glycolipid/water system. *Langmuir* **12**, 5250–5253 (1996).
20. G. Ungar, X. Zeng, Frank-Kasper, quasicrystalline and related phases in liquid crystals. *Soft Matter* **1**, 95–106 (2005).
21. D. V. Perronic, M. K. Mahanthappa, Inverse Pm3n cubic micellar lyotropic phases from zwitterionic triazolium gemini surfactants. *Soft Matter* **9**, 7919–7922 (2013).
22. C. M. Baez-Cotto, M. K. Mahanthappa, Micellar mimicry of intermetallic C14 and C15 Laves phases by aqueous self-assembly. *ACS Nano* **12**, 3226–3234 (2018).
23. M. Huang *et al.*, Selective assemblies of giant tetrahedra via precisely controlled positional interactions. *Science* **348**, 424–428 (2015).
24. K. Yue *et al.*, Geometry induced sequence of nanoscale Frank-Kasper and quasicrystal mesophases in giant surfactants. *Proc. Natl. Acad. Sci. U.S.A.* **113**, 14195–14200 (2016).
25. Z. Su *et al.*, Identification of a Frank-Kasper Z phase from shape amphiphile self-assembly. *Nat. Chem.* **11**, 899–905 (2019).
26. G. M. Grason, B. A. DiDonna, R. D. Kamien, Geometric theory of diblock copolymer phases. *Phys. Rev. Lett.* **91**, 058304 (2003).
27. N. Xie, W. Li, F. Qiu, A. C. Shi, σ phase formed in conformationally asymmetric AB-type block copolymers. *ACS Macro Lett.* **3**, 906–910 (2014).
28. M. W. Schulze *et al.*, Conformational asymmetry and quasicrystal approximants in linear diblock copolymers. *Phys. Rev. Lett.* **118**, 207801 (2017).
29. A. Reddy *et al.*, Stable Frank-Kasper phases of self-assembled, soft matter spheres. *Proc. Natl. Acad. Sci. U.S.A.* **115**, 10233–10238 (2018).
30. S. Lee, C. Leighton, F. S. Bates, Sphericity and symmetry breaking in the formation of Frank-Kasper phases from one component materials. *Proc. Natl. Acad. Sci. U.S.A.* **111**, 17723–17731 (2014).
31. R. M. Lewis III *et al.*, Role of chain length in the formation of Frank-Kasper phases in diblock copolymers. *Phys. Rev. Lett.* **121**, 208002 (2018).
32. A. P. Lindsay *et al.*, A15, σ and a quasicrystal: Access to complex particle packings via bidisperse diblock copolymer blends. *ACS Macro Lett.* **9**, 197–203 (2020).
33. M. Liu, Y. Qiang, W. Li, F. Qiu, A. C. Shi, Stabilizing the Frank-Kasper phases via binary blends of AB diblock copolymers. *ACS Macro Lett.* **5**, 1167–1171 (2016).
34. W. Li, C. Duan, A. C. Shi, Nonclassical spherical packing phases self-assembled from AB-type block copolymers. *ACS Macro Lett.* **6**, 1257–1262 (2017).
35. H. Takagi, K. Yamamoto, Phase boundary of Frank-Kasper σ phase in phase diagrams of binary mixtures of block copolymers and homopolymers. *Macromolecules* **52**, 2007–2014 (2019).
36. A. J. Mueller *et al.*, Emergence of a C15 Laves phase in diblock polymer/homopolymer blends. *ACS Macro Lett.* **9**, 576–582 (2020).
37. A. N. Semenov, Phase equilibria in block copolymer-homopolymer mixtures. *Macromolecules* **26**, 2273–2281 (1993).
38. M. Zhao, W. Li, Laves phases formed in the binary blend of AB₄ miktoarm star copolymer and a homopolymer. *Macromolecules* **52**, 1832–1842 (2019).
39. S. Chanpuriya *et al.*, Cornucopia of nanoscale ordered phases in sphere-forming tetrablock terpolymers. *ACS Nano* **10**, 4961–4972 (2016).
40. A. Arora, N. Pillai, F. S. Bates, K. D. Dorfman, Predicting the phase behavior of ABAC tetrablock terpolymers: Sensitivity to Flory-Huggins interaction parameters. *Polymer* **154**, 305–314 (2018).
41. A. Arora *et al.*, Broadly accessible self-consistent field theory for block polymer materials discovery. *Macromolecules* **49**, 4675–4690 (2016).
42. S. Koizumi, H. Hasegawa, T. Hashimoto, Spatial distribution of homopolymers in block copolymer microdomains as observed by a combined SANS and SAXS method. *Macromolecules* **27**, 7893–7906 (1994).
43. H. G. Peng *et al.*, Distributions of a linear homopolymer additive in an ordered block copolymer matrix as quantified by small-angle neutron scattering. *Macromolecules* **48**, 7574–7584 (2015).
44. Y. Tamai, R. Sekine, H. Aoki, S. Ito, Conformation of single homopolymer chain in microphase-separated block copolymer monolayer studied by scanning near-field optical microscopy. *Macromolecules* **42**, 4224–4229 (2009).
45. A. Arora, D. C. Morse, F. S. Bates, K. D. Dorfman, Accelerating self-consistent field theory of block polymers in a variable unit cell. *J. Chem. Phys.* **146**, 244902 (2017).
46. M. W. Matsen, Phase behavior of block copolymer/homopolymer blends. *Macromolecules* **28**, 5765–5773 (1995).