Macromolecular Metallurgy of Binary Mesocrystals via Designed Multiblock Terpolymers

Nan Xie,[†,‡] Meijiao Liu,[†,‡] Hanlin Deng,[†,‡] Weihua Li,*[†] Feng Qiu,[†] and An-Chang Shi[§]

[†]State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China

[§]Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada, L8S 4M1

Ⓢ *Supporting Information*

ABSTRACT: Self-assembling block copolymers provide access to the fabrication of various ordered phases. In particular, the ordered spherical phases can be used to engineer soft mesocrystals with domain size at the 5−100 nm scales. Simple block copolymers, such as diblock copolymers, form a limited number of mesocrystals. However multiblock copolymers are capable to form more complex mesocrystals. We demonstrate that designed $B_1AB_2CB_3$ multiblock terpolymers, in which the A- and C-blocks form spherical domains and the packing of these spheres can be controlled by changing the lengths of the middle and terminal B-blocks, self-assemble into various binary mesocrystals with space group symmetries of a large number of binary ionic crystals, including NaCl, CsCl, ZnS, α-BN, AlB_2, CaF_2, TiO_2, ReO_3, Li_3Bi, Nb_3Sn(A15), and α-Al_2O_3. This approach can be generalized to other terpolymers as well as to tetrapolymers to obtain ternary mesocrystals. Our study provides a new concept of macromolecular metallurgy for producing crystal phases in a mesoscale and thus makes multiblock copolymers a robust platform for the engineering of functional materials.

Crystals are extremely attractive materials because of their rich symmetries and exceptional mechanical, electronic, and optical properties. For the fabrication of functional materials, ordered crystalline structures with feature sizes from nanometer to micrometer, which are beyond that of hard atomic crystals, are required in order to satisfy a wide range of application needs. Examples include lithographic templates of high-density magnetic storage media, quantum dots, photonic crystals, and catalysis scaffolds.[1−4] These crystal structures can be generated by self-assembly of either nanoscale inorganic colloids[5,6] or macromolecules, such as amphiphilic liquid crystals (LCs)[7−11] and block copolymers (BCPs).[12−15] Very recently, a general method of preparing DNA-programmable atom equivalents (PAEs) for achieving diverse colloidal crystals has been proposed by Zhang et al.[16] Alternatively, the self-assembly of macromolecules (LCs or BCPs) provides direct access to the formation of soft mesocrystals, which are composed of spherical domains arranged on crystalline lattice. Importantly, the feature size of the mesocrystals can be readily tuned by the molecular weight of the macromolecules. On the other hand, both amphiphilic LCs and BCPs with simple molecular architectures only self-assemble into

a very limited set of crystal structures. For example, binary crystals with the symmetries of NaCl, ZnS, and AlB_2 have been obtained from inorganic colloidal systems[5,6,17] but have not yet been obtained in BCPs. In what follows we will explore the feasibility of using designed BCPs to obtain ordered phases with symmetries of binary crystals.

It has been demonstrated that multiblock copolymers offer unparalleled opportunities for the formation of complex ordered phases. At the same time, it has been argued that multiblock copolymers could possibly become a Pandora's Box without a valid design principle of architectures because of their drastically increased phase complexity.[18] Normally, polymer chemists synthesize new macromolecules and then explore into which structures they self-assemble. In view of the high dimensionality of macromolecular parameter space (e.g., chain topology, number and sequence of blocks, incompatibilities), it is more efficient to use theory and computation to derive guiding principles of rationally designed macromolecules for the formation of targeted structures. The combination of theoretical modeling and experiments can then lead to a platform of macromolecular metallurgy (MM) for recasting crystal phases with BCPs in a mesoscale.

Spherical domains self-assembled from macromolecules can be viewed as artificial macromolecular "atoms" (AMAs) (Figure 1a). These AMAs are soft, thereby having different packing mode from hard spheres which usually adopt the crystal lattice of face-centered cubic with $Fm\bar{3}m$ symmetry or hexagonal close packing (hcp) with $P6_3/mmc$ symmetry. It has been known that the simplest diblock copolymers mainly self-assemble into the body-centered cubic (bcc) phase with $Im\bar{3}m$ symmetry and only have a very tiny hcp phase region near the order−disorder transition (ODT) boundary.[19,20] When the molecular architecture is modified to be a miktoarm star-type of AB_n with the minority A-block, another cubic phase, A15 lattice with $Pm\bar{3}n$ symmetry, becomes stable and occupies a phase region between bcc and hexagonal cylinder phase (Hex) with varying A composition.[21,22] The A15 phase has since been found in many dentritic[7−11] or other amphiphilic compounds.[23] In addition, a more complex noncubic sphere phase, a tetragonal lattice with a large unit cell and $P4_2/mnm$ symmetry, which was referred to as the σ phase by Frank and Kasper many years ago, has been observed in one dentritic amphiphilic compound.[9] Recently, the σ phase has been observed in two BCP samples by Lee et al.[15] Although the A15
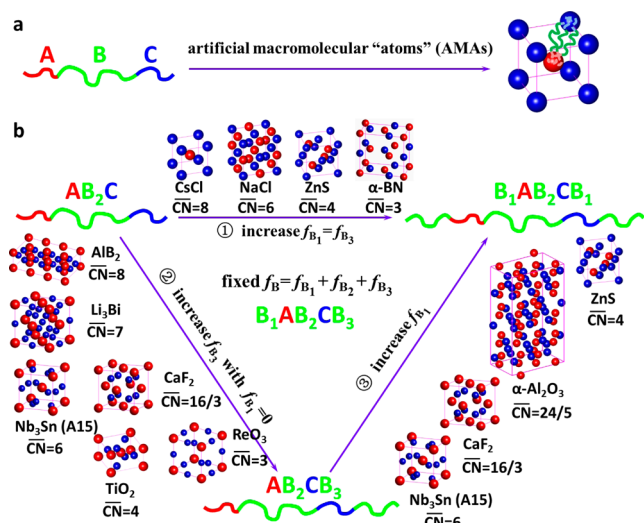
Figure 1. Design principle of multiblock terpolymers for binary soft mesocrystals. (a) AMAs self-assembled by linear ABC triblock copolymers pack into the CsCl crystal lattice. (b) AMAs formed by multiblock terpolymers can be programmed to assemble into a variety of crystallographic arrangements by tailoring the polymer architectures. Three possible paths are demonstrated as design series of mesocrystals with varying magnitude and asymmetry of coordination numbers (CNs) by tuning the relative lengths among B-blocks while keeping the total B component fixed.

and σ phases were first observed in binary transition-metal alloys,[11,24] there is only one-component AMA in above macromolecular samples. Identification of these complex phases presents the opportunity for designing useful mesocrystals via macromolecular self-assembly.[15,25]

Besides the one-component crystals, there are a large number of binary crystals, such as ionic crystals and binary metal alloys. These crystals provide a vast library of structure prototypes. From the perspective of both potential applications and fundamental interest, it is interesting and challenging to design mesocrystals of those structure prototypes by BCP self-assembly. In order to form binary crystals, three-component BCP is needed, in which the two minority blocks self-assemble into spheres and the majority blocks form the matrix. One of the simplest three-component BCPs is a linear ABC triblock copolymer with equal A- and C-blocks forming A and C AMAs. Theoretical studies revealed that the CsCl structure occupies most of the phase region where spheres form, and the NaCl structure is only stable in an extremely narrow range of interaction parameters, $\chi_{ij}N$ (i, j = A, B, C), where N is the total degree of polymerization.[26,27] These previous studies demonstrated that the virtually limitless variations of terpolymer architectures could provide a platform to obtain various binary crystal phases. Nevertheless, a systematic approach of designing BCPs for the fabrication of diverse binary mesocrystals is required in order to prevent the system becoming a Pandora's Box.

In this report, we propose a design principle for the formation of binary mesocrystals using BCPs. The basic idea is to utilize two or more minority blocks to form the spherical domains, or AMAs, and to use the majority blocks to control the packing of the AMAs. We demonstrate the feasibility and capability of this approach by examining the phase diagram of multiblock terpolymers $B_1AB_2CB_3$, focusing on the cases where the A- and C-blocks form spheres or AMAs. The sizes and effective valencies

of the AMAs, quantified by the magnitude (or average value of CNs, $\overline{CN}$) and asymmetry of coordination numbers (CNs), are modulated by the relative lengths of the middle and terminal B-blocks (Figure 1b). A variety of soft binary mesocrystals with variable symmetries, along with some nonspherical phases, are predicted using the self-consistent field theory (SCFT).[28]

There are a large number of parameters in the terpolymer systems. To reduce the parameter space as well as to make the calculations feasible, a number of parameters are kept at constant in the calculations: $\chi_{AB}N = \chi_{BC}N = \chi_{AC}N = 80$, $f = f_A = f_C$ (volume fractions of A- and C-blocks) and equal segment sizes. Within this restricted phase space, we can divide the system into three typical cases by additional constraints: (1) symmetric-tail pentablock terpolymer with $f_{B1} = f_{B3}$ ($B_1AB_2CB_1$), (2) complete asymmetric-tail tetrablock with $f_{B1} = 0$ (AB_2CB_3), and (3) asymmetric-tail pentablock with $f_{B1} < f_{B3}$ for a given $f_A = f_C = 0.10$ ($B_1AB_2CB_3$). Accordingly, the independent controlling parameters of the first two cases are (f, f_{B2}) and that of the third case are (f_{B2}, γ), where $\gamma = f_{B1}/f_{B3}$.

For the symmetric-tail terpolymer, $B_1AB_2CB_1$, the A- and C-spheres must pack into equivalent lattices and thus have equal CNs. The corresponding phase diagram in the f–f_{B2} plane is presented in Figure 2. The transition points are determined by
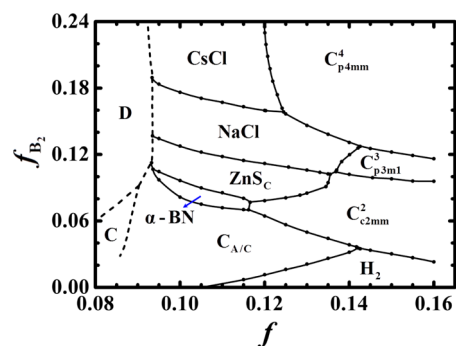

Figure 2. Phase diagram in the f–f_{B2} plane for symmetric-tail $B_1AB_2CB_1$ terpolymers with fixed $\chi N = 80$. The filled circles denote the points where we have calculated the phase boundaries, and the solid lines are a guide for the eyes. The dashed lines indicate the estimated order–disorder transition boundaries.

comparison of the free energy of the different phases, which is obtained from SCFT calculations using the pseudospectral method[29,30] together with Anderson mixing iteration-accelerating scheme.[31] The calculation details are given in the Supporting Information (SI). For increasing f_{B1} or decreasing f_{B2} at a fixed $f = 0.10$ along the path 1 in Figure 1b, a phase transition sequence of CsCl, NaCl, ZnS sphalerite (ZnS_C), layered honeycomb structure of α-BN, and hexagonal cylinders consisting A/C alternative domains ($C_{A/C}$) is predicted by the SCFT. Some of the ordered phases are nonspherical phases. Obviously the CNs of these mesocrystals decrease along this path (symmetries and CNs are listed in Table S1). In the α-BN structure, the A- and C-spheres are alternatively stacked along the direction normal to layers, within which each A- or C-sphere is triply coordinated by their counterparts. Between the layers, there are rarely bridges formed by the short B_2-block. Therefore α-BN has an effective CN = 3. This structure is analogous to the graphite structure if the bridging interaction is viewed as a covalent bond and the weak nonbridging interaction is viewed as van der Waals interaction. The stable phase of the $B_1AB_2CB_1$ terpolymers is CsCl when f_{B1} is negligibly small.[26,27] The polyhedral shape of

the Voronoi cell of the crystal with a higher CN deviates less from ideal sphere and thus has more favorable interfacial energy (see Figure S2).[21] The advantage of interfacial energy falls off when the spherical domain shrinks. As f_{B2} decreases, the A-C spheres are pulled closer and closer (shown in Figure S4), and the sphere size is decreased because of the volume conservation. Smaller spherical domains containing less polymer chains result in higher interfacial energy. Because the sphere size in the crystal lattice with a higher CN is smaller for a given sphere−sphere distance, l_{AC}, and drops down more rapidly (more details are presented in SI), the penalty of interfacial energy is more severe in CsCl than NaCl (see Figure S1b). As a result, the CsCl structure transfers to NaCl when the B_2-block is reduced below 0.18. Meanwhile, the sequence of transitions is accompanied by a release of stretching of the B_2-block (see Figure S3). A similar phase sequence with decreasing tendency of CNs is shown in the two-dimensional cylindrical phase region, where the transition sequence is C_{p4mm}^4 with CN = 4, C_{p3m1}^3 with CN = 3, C_{c2mm}^2, and a hexagonally packed double-strand helical phase H_2, within which each helix is composed of a pair of A/C strands twining around each other (see Table S1). H_2 is different from the helical structure formed in frustrated ABC terpolymers, where two B-formed cylinders twine around a central C cylinder.[32] These results lead us to conclude that the length of the middle B-block can be used to control the CNs of the structures. This conclusion can be used as one designing principle for the $B_1AB_2CB_3$ terpolymers.

Many binary ionic crystals or metallic alloys have unequal CNs. In the complete asymmetric-tail AB_2CB_3 terpolymers, the free end of the A-block can stay anywhere inside an A-sphere, while C-block has to keep its two junctions on the surface of the C-sphere and thus inducing an extra stretching of the C-blocks. In this case forming a smaller C-sphere than A-sphere is the only way to release this extra stretching. With $f = f_A = f_C$, the binary phases prefer to adopt more C-spheres than A-spheres, i.e., to have a larger CN of A than C. When a small B_1-block is added to the A-end, the CN asymmetry can be reduced. The phase diagram of (f, f_{B2}) for AB_2CB_3 is given in Figure 3. Similarly, the phase sequence with declining $\overline{CN}$ is seen in both sphere and cylinder phases when decreasing f_{B2} along the path 2 in Figure 1b. At the phase region of small f, abiding by the proposed guiding principle, there exists a phase sequence of CsCl, AlB_2,
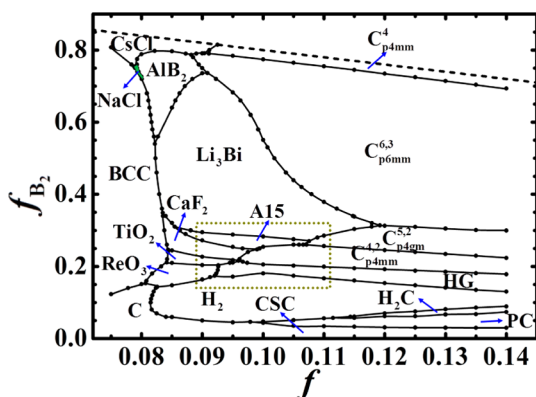
$C_{p6mm}^{6,3}$, Li_3Bi, Nb_3Sn (A15), CaF_2, TiO_2, ReO_3, helical super-cylinder H_2, and hexagonal core−shell cylinder CSC. In the region of cylinder phases, a number of intriguing phases are obtained, including $C_{p6mm}^{6,2}$, $C_{p4gm}^{5,2}$, $C_{p4mm}^{4,2}$, perforated supercylinder PC, and hierarchical gyroid phase HG. The general sequence of cylinder phases is C_{p4mm}^4, $C_{p6mm}^{6,3}$, $C_{p6mm}^{6,2}$ (occupying a very tiny region), $C_{p4gm}^{5,2}$, and $C_{p4mm}^{4,2}$. The $C_{p6mm}^{6,3}$ phase was first reported with a linear SBM terpolymer 15 years ago,[33] and it was re-identified precisely by a resonant soft X-ray scattering with a linear IS2VP terpolymer.[34] In fact, the $C_{p6mm}^{6,3}$ phase is not a stable phase in the simple ABC terpolymer with the present parameters. However, when a slight asymmetry is introduced by adding a small B-block onto the end of C-block to form ABCB tetrablock, $C_{p6mm}^{6,3}$ occupies a significant phase region at the cost of the C_{p4mm}^4 structure. These two-dimensional cylindrical morphologies with symmetries of p4mm, p6mm, and p4gm, have been observed in bolaamphiphilic LCs with a lateral chain, where the pattern symmetry is simply modulated by the length of lateral chain.[35] The predominant factor in the two systems is fairly similar, i.e., to fill the outside space of spheres under the framework of crystal lattices with a given lattice constant using varying amount of matter (end blocks or lateral chains). Based on these results, we can also design interesting series of mesocrystals when one or a few lateral B-blocks are used to replace the end blocks.

There are two competing factors in phase transitions: the average magnitude of CNs determined by the length of the middle B_2-block and the asymmetric degree of CNs depending on the architecture asymmetry. The symmetric and asymmetric terpolymers discussed above are two limits. On the other hand, the asymmetric degree can be varied continuously by modifying the relative lengths of the two end B-blocks in $B_1AB_2CB_3$, which allows us to examine the change of CNs from symmetric to asymmetric. The phase diagram in the (f_{B2}, γ) plane for fixed $f = 0.10$ is given in Figure 4. The path 3 in Figure 1b, along which the

Figure 3. Phase diagram in the $f-f_{B2}$ plane for AB_2CB_3 terpolymers with fixed $\chi N = 80$. The top dashed line indicates the limit of AB_2C triblock. The very tiny NaCl region is filled with green color. Here bcc and C represent the simple bcc sphere and hexagonal cylinder phases, respectively, where A- and C-blocks do not phase separate. The portion inside the dotted line box is enlarged in Figure S7.
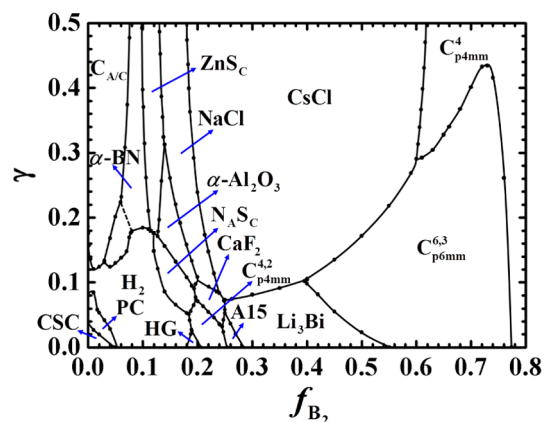

Figure 4. Phase diagram as function of f_{B2} and $\gamma = f_{B1}/f_{B3}$ for $B_1AB_2CB_3$ pentablock terpolymers with fixed $\chi N = 80$ and $f = 0.10$. α-BN at the bottom of the region transforms continuously into a new phase (denoted as α-nBN in Table S1) by fusing isolated A domains into layered network when the molecular asymmetry is added, and therefore the transition curve is plotted with dashed lines.

phase sequence with decreasing $\overline{CN}$ and CN asymmetry is comprised of A15, CaF_2, α-Al_2O_3, and ZnS_C, is identified in this phase diagram. One notable intriguing feature is that the complex phase of rhombohedral α-Al_2O_3 corundum becomes stable and has a noticeable region of $0.1 \lesssim \gamma \lesssim 0.32$ locating between the ZnS_C and NaCl structures. This indicates that the asymmetric

degree of CN is much smaller than that between two end blocks because one-dimensional chains are packed into three-dimensional domains. Additionally, the presence of the α-Al$_2$O$_3$ structure foretells the possibility of a new binary cylinder pattern with a small CN asymmetry of 2:3 if varying γ in the phase region of cylinders. Besides sphere crystals, a few new phases like N$_A$S$_C$ and α-nBN are identified (see Table S1).

In summary, the current study demonstrates a simple valid principle for the fabrication of binary mesocrystalline phases via the self-assembly of multiblock B$_1$AB$_2$CB$_3$ terpolymers, in which the middle B-block is used to control the coordination number and size of the A and C spherical domains. At the same time, the end B-blocks are introduced to ensure a fixed total B composition on the one hand and to modulate the asymmetric degree of CNs via varying their relative lengths on the other hand. This design principle can be generalized to the fabrication of ternary mesocrystals using multiblock tetrapolymers. This theoretical study presented in this paper serves as a starting point for the establishment of a platform for the macromolecular metallurgy of mesocrystals via the self-assembly of multiblock copolymers. At the same time, the current study provides a compelling example in which multiblock copolymers can be considered more likely a panacea than a Pandora's Box in materials design.[18] With the development of precise synthesis techniques, more complex multiblock terpolymers have been synthesized, such as the VISISISISIV undecablock,[36] CECEC-P hexablock,[37] and SISO tetrablock terpolymers.[15,38] In particular, the SISO tetrablock terpolymer is quite similar to the complete asymmetric-tail terpolymer sample when the composition of PI block is reduced to form spheres. The availability of these complex multiblock copolymers makes it possible to explore the theoretically predicted crystal phases by experiments.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Theoretical methods, Tables S1−S4, and Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
weihuali@fudan.edu.cn

Author Contributions
‡These authors contributed equally.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Park, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401.

(2) Chan, V. Z. H.; Hoffman, J.; Lee, V. Y.; Iatrou, H.; Avgeropoulos, A.; Hadjichristidis, N.; Miller, R. D.; Thomas, E. L. *Science* **1999**, *286*, 1716.

(3) Thurn-Albrecht, T.; Schotter, J.; Kastle, C. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. *Science* **2000**, *290*, 2126.

(4) Lopes, W. A.; Jaeger, H. M. *Nature* **2001**, *414*, 735.

(5) Vermolen, E. C. M.; Kuijk, A.; Filion, L. C.; Hermes, M.; Thijssen, J. H. J.; Dijkstra, M.; van Blaaderen, A. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 16063.

(6) Dong, A. G.; Chen, J.; Vora, P. M.; Kikkawa, J. M.; Murray, C. B. *Nature* **2010**, *466*, 474.

(7) Hudson, S.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, V. *Science* **1997**, *278*, 449.

(8) Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D.; Möller, M.; Sheiko, S. *Nature* **1998**, *391*, 161.

(9) Ungar, G.; Liu, Y.; Zeng, X.; Percec, V.; Cho, W.-D. *Science* **2003**, *299*, 1208.

(10) Percec, V.; Mitchell, C. M.; Cho, W.-D.; Uchida, S.; Glodde, M.; Ungar, G.; Zeng, X.; Liu, Y.; Balagurusamy, V. S.; Heiney, P. A. *J. Am. Chem. Soc.* **2004**, *126*, 6078.

(11) Ungar, G.; Zeng, X. *Soft Matter* **2005**, *1*, 95.

(12) Hillmyer, M. A.; Bates, F. S.; Almdal, K.; Mortensen, K.; Ryan, A. J.; Fairclough, J. P. A. *Science* **1996**, *271*, 976.

(13) Hamley, I. W. *The Physics of Block Copolymers*; Oxford Univ. Press: Oxford, 1998.

(14) Bang, J.; Jeong, U.; Ryu, D. Y.; Russell, T. P.; Hawker, C. J. *Adv. Mater.* **2009**, *21*, 4769.

(15) Lee, S.; Bluemle, M. J.; Bates, F. S. *Science* **2010**, *330*, 349.

(16) Zhang, C.; Macfarlane, R. J.; Young, K. L.; Choi, C. H. J.; Hao, L. L.; Auyeung, E.; Liu, G. L.; Zhou, X. Z.; Mirkin, C. A. *Nat. Mater.* **2013**, *12*, 741.

(17) Maldovan, M.; Thomas, E. L. *Nat. Mater.* **2004**, *3*, 593.

(18) Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H. *Science* **2012**, *336*, 434.

(19) Matsen, M. W.; Schick, M. *Phys. Rev. Lett.* **1994**, *72*, 2660.

(20) Matsen, M. W. *J. Phys.: Condens. Matter* **2002**, *14*, R21.

(21) Grason, G. M.; DiDonna, B.; Kamien, R. D. *Phys. Rev. Lett.* **2003**, *91*, 058304.

(22) Grason, G. M.; Kamien, R. D. *Macromolecules* **2004**, *37*, 7371.

(23) Cheng, X. H.; Diele, S.; Tschierske, C. *Angew. Chem., Int. Ed.* **2000**, *39*, 592.

(24) Sinha, A. K. *Topologically Close Packed Structures in Transition Metal Alloys*; Pergamon Press: Oxford, 1972.

(25) Peterca, M.; Percec, V. *Science* **2010**, *330*, 333.

(26) Matsen, M. W. *J. Chem. Phys.* **1998**, *108*, 785.

(27) Qin, J.; Bates, F. S.; Morse, D. C. *Macromolecules* **2010**, *43*, 5128.

(28) Fredrickson, G. H. *The Equilibrium Theory of Inhomogeneous Polymers*; Oxford Univ. Press: Oxford, 2006.

(29) Rasmussen, K. ø.; Kalosakas, G. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 1777.

(30) Tzeremes, G.; Rasmussen, K. ø.; Lookman, T.; Saxena, A. *Phys. Rev. E* **2002**, *65*, 041806.

(31) Thompson, R. B.; Rasmussen, K. ø.; Lookman, T. *J. Chem. Phys.* **2004**, *120*, 31.

(32) Li, W. H.; Qiu, F.; Shi, A. C. *Macromolecules* **2012**, *45*, 503.

(33) Brinkmann, S.; Stadler, R.; Thomas, E. L. *Macromolecules* **1998**, *31*, 6566.

(34) Wang, C.; Lee, D. H.; Hexemer, A.; Kim, M. I.; Zhao, W.; Hasegawa, H.; Ade, H.; Russell, T. P. *Nano Lett.* **2011**, *11*, 3906.

(35) Tschierske, C. *Chem. Soc. Rev.* **2007**, *36*, 1930.

(36) Masuda, J.; Takano, A.; Nagata, Y.; Noro, A.; Matsushita, Y. *Phys. Rev. Lett.* **2006**, *97*, 098301.

(37) Fleury, G.; Bates, F. S. *Macromolecules* **2009**, *42*, 1691.

(38) Zhang, J.; Bates, F. S. *J. Am. Chem. Soc.* **2012**, *134*, 7636.