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Process-accessible states of block copolymers

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Process-directed self-assembly of block copolymers refers to thermodynamic processes that reproducibly direct the kinetics of structure formation from a starting, unstable state into a selected, metastable mesostructure. We investigate the kinetics of self-assembly of linear ACB triblock copolymers after a rapid transformation of the middle C -block from B to A . This prototypical process (e.g., photochemical transformation) converts the initial, equilibrium mesophase of the ABB copolymer into a well-defined but unstable, starting state of the AAB copolymer. The spontaneous structure formation that ensues from this unstable state becomes trapped in a metastable mesostructure, and we systematically explore, which metastable mesostructures can be fabricated by varying the block copolymer composition of the initial and final states. In addition to the equilibrium mesophases of linear AB diblock copolymers, this diagram of process-accessible states includes 7 metastable periodic mesostructures; inter alia, Schoen's F-RD periodic minimal surface. Generally, we observe that the final, metastable mesostructure of the AAB copolymer possesses the same symmetry as the initial, equilibrium mesophase of the ABB copolymer.

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The spontaneous formation of periodically ordered mesostructures with characteristic dimensions of 5 – 100 nm is the most characteristic and fascinating ability of block copolymers [1–3]. The stability of these self-assembled mesostructures is governed by a subtle balance of the interfacial tension between different domains and conformational stretching entropy [4]. For the deceptively simple, linear AB diblock copolymer melt, six spatially modulated mesophases, including close-packed spheres (CPS) [52], body-centered-cubic spheres (BCC), hexagonally packed cylinders (HEX), cubic gyroid networks (GYR), orthorhombic $Fddd$ networks (O^{70}), and lamellae (LAM), are thermodynamically stable, equilibrium states as a function of the volume fraction, f_A , of A -segments and the incompatibility, $\chi_{AB}N$ [4–7].

The free-energy landscape of diblock copolymers, however, is even more complex and features a multitude of metastable free-energy minima, e.g., alternate periodic mesostructures such as the hexagonally perforated lamellae (HPL) [1], grain boundaries, and localized defects [8]. In fact, the free-energy landscape has been likened to that of glass formers [9]. Although these mesostructures are only metastable, the free-energy barriers that separate them typically scale like $\sqrt{N}k_B T$ [10, 11]. Thus, a large invariant degree of polymerization, N , results in protracted lifetimes of minutes or hours, which suffice to additionally stabilize the mesostructures by cooling below the glass-transition temperature or crosslinking. In spite of the ubiquitous occurrence of metastable mesostructures in the course of self-assembly and the abiding interest in equilibrium mesophases and metastable mesostructures [12–17], the *kinetic pathways* that lead to the formation of desired, non-equilibrium mesostructures are rather less explored [18–20].

In this Letter we systematically investigate a prototyp-

ical class of thermodynamic processes that start from an equilibrium mesophase and reproducibly prepare a well-defined, unstable, starting state. We design the processes so that the spontaneous structure formation that ensues from this so-prepared, starting, unstable state becomes finally trapped into a selected, metastable state and devise a diagram of process-accessible mesostructures. This diagram provides valuable insights into the complex free-energy landscape of these soft-matter systems and, potentially, enables the reproducible fabrication of novel mesostructures without the need to synthesize new complex chain architectures.

As a first exploratory step, we investigate a simple thermodynamic process: We consider an incompressible melt of linear ACB triblock copolymers where the chemo-physical properties of the middle block, C , can be rapidly altered. At the beginning, the C -block is miscible with the B -block and, for simplicity, we set $\chi_{BC} = 0$ and $\chi_{AB} = \chi_{AC} > 0$. Thus, the initial state is an equilibrium mesophase of the ABB system. Then the process renders the C -block thermodynamically compatible with the A -block and, specifically, we set $\chi_{AB} = \chi_{BC} > 0$ and $\chi_{AC} = 0$. In addition, we assume that the conversion of the C -block is fast compared to the structural relaxation of the chain conformations. Such an alchemical transformation of the C -block from B to A could potentially be realized e.g., by a photochemical reaction [53]. Whereas this specific thermodynamic process certainly is highly idealized, it is well suited to illustrate the concept of process-directed self-assembly and its potential for fabricating novel mesostructures, and to devise general correlations between the initial, equilibrium mesophase of the ABB system and the final, metastable mesostructure of the AAB system after the process.

In the following, we consider $\chi_{AB}N = 23$, where N

FIG. 2: Graphical representations of final mesostructures – (a) FCC, (b) F-RD, (c) BCC, (d) I-WP, (e) I-WP-S, (f) HEX, (g) HEX2*, (h) GYR-S, (i) GYR, (j) DIA, (k) DIA-S, (l) LAM – that can be fabricated by process-directed self-assembly using an alchemical conversion of the middle C -block.

to the equilibrium mesophase, whereas for large f_A^* the HEX, GYR, or LAM mesophase, respectively, represents the absolute minimum of the free-energy landscape.

Upon increasing f_A^* further, the character of the final, metastable mesostructure gradually changes because the A -density between the enlarged A -spheres increases and makes the A -spheres become connected. Joining the A -spheres between the first nearest neighbors results in the formation of the metastable I-WP mesostructure that is depicted in Fig. 2d. We emphasize that this change of the final, metastable mesostructure from BCC to I-WP upon the increase of f_A^* is completely gradual, and it is not associated with a change between free-energy basins; merely the character of the basin smoothly varies with f_A^* . Thus, BCC and I-WP are not thermodynamically different mesostructures and the location of the smooth crossover is indicated by a horizontal, blue, dashed line in this diagram.

Upon increasing f_A^* still further, i.e., for $f_A^* \geq \frac{99}{128}$, the B -domains gradually break up into spheres and the metastable I-WP-S mesostructure, which is presented in Fig. 2e, is fabricated. Note that the alchemical conversion process does not result in a change of the basin on the free-energy landscape for all these values of f_A^* . This feature also explains why the final, metastable mesostructure is insensitive to the details of the DSCFT.

Only for $f_A = \frac{28}{128} \rightarrow f_A^* \geq \frac{102}{128}$ does the alchemical conversion process result in a basin change; in this case, the final, metastable mesostructure is the disordered state and the concomitant transition is marked by a horizontal, black, solid line in this diagram. Note that in the interval $\frac{102}{128} \leq f_A^* < 0.814387$ the disordered

state is only metastable; the thermodynamic equilibrium mesophases are BCC and FCC mesostructures, respectively, depending on the value of f_A^* .

In addition to the known thermodynamic equilibrium mesophases, the diagram of process-accessible states, Fig. 1, comprises 7 additional metastable mesostructures: There are three bicontinuous network mesostructures, Schoen’s F-RD [47, 48], Schoen’s I-WP [47, 49], and the cubic single-DIAmond network (DIA) [50], as well as the graphene-like arrangement of cylindrical domains in the HEX2* mesostructure [51] and different arrangements of spherical domains, I-WP-S, GYR-S, and DIA-S. This diagram also contains a FCC* mesostructure where the B -block forms the spherical domains that arrange on a FCC-lattice (see in the Supplemental Material), which is shifted with respect to the FCC-lattice of the initial, equilibrium mesophase shown in Fig. 2a.

To the best of our knowledge, the metastable F-RD [57], I-WP-S, GYR-S, and DIA-S [58] mesostructures have not yet been experimentally observed.

Generally, the alchemical conversion process does not result in a change of free-energy basin and, consequently, the final, metastable mesostructure at f_A^* possesses the same symmetry as the initial, equilibrium mesophase at f_A . Thus, the sequence of final, metastable mesostructures upon varying f_A^* markedly differs from the sequence of equilibrium mesophases. For example, the alchemical conversion processes of the initial, equilibrium mesophase at $f_A = \frac{28}{128}$ yield the sequence of BCC, I-WP, I-WP-S, and DIS mesostructures upon increasing f_A^* , whereas the corresponding equilibrium mesophases are BCC, HEX, GYR, LAM, GYR, HEX, BCC, FCC, and DIS [4].

Notable exceptions from this general observation are alchemical transformations of long C -blocks, i.e., large $|f_A^* - f_A|$, which catapult the starting, unstable state out of the free-energy basin of the initial, equilibrium mesophase. The new basin can be the basin of the DIS mesostructure, or the basin of another spatially modulated mesostructure. There are two examples of the latter: the process-directed self-assembly from the initial, equilibrium GYR mesophase to the final, metastable DIA mesostructure and from the initial, equilibrium FCC mesophase to the final, metastable FCC* mesostructure. In the following, we focus on the case of the metastable DIA mesostructure. The case of the metastable FCC* mesostructure is discussed in the Supplemental Material.

To validate the DSCFT calculations we perform SCMF simulations of a soft, particle-based model with $N = 32$ coarse-grained segments per macromolecule. The softness allows us to represent a large invariant degree of polymerization, $\sqrt{N} = 128000$. For $f_A = \frac{11}{32}$, we equilibrate an equilibrium gyroid network in a cubic simulation cell of linear dimension $11.979R_{e0}$ with periodic boundary conditions. At frozen chain conformations, we switch the A -volume fraction to $f_A^* = \frac{22}{32}$ by converting the identity of the 11 middle segments from B to A . The

FIG. 3: Time evolution observed by SCMF simulations after an alchemical conversion process of an equilibrium gyroid network from $f_A = \frac{11}{32}$ to $f_A^* = \frac{22}{32}$ at $\chi_{AB}N = 23$. The different panels show the A -density (red color) at different times measured in units of Monte-Carlo (MC) steps per segment. The simulation cell totally comprises 27 cubic unit cells.

spontaneous structure formation from this starting, unstable state is shown in Fig. 3. First, around 1000 MC steps, we observe the formation of an A -gyroid network, which subsequently transforms into the DIA mesostructure of B -channels around 5000 MC steps, which approximately correspond to half of the time a polymer chain in a disordered melt needs to diffuse a distance R_{e0} . The system only evolves slowly during the simulation runs that has been extended up to 15 000 MC steps, indicating the metastability of the DIA mesostructure. A similar time evolution is also observed in both, non-conserved and conserved, DSCFT calculations.

To further illustrate the process-directed self-assembly of the metastable DIA mesostructure by an alchemical conversion process, we present in Fig. 4 the free energies of the GYR and DIA mesostructures as a function of f_A^* . In the interval $\frac{52}{128} \leq f_A^* \leq \frac{87}{128}$, both GYR and DIA mesostructures are metastable at the periodicity, $L^{\text{init}} = 3.993R_{e0}$ that is dictated by the value of the initial, equilibrium GYR mesophase at $f_A = \frac{44}{128}$. For $f_A^* \leq \frac{86}{128}$, the process-directed self-assembly yields the metastable GYR mesostructure, which resides inside the free-energy basin of the initial, equilibrium mesophase. As f_A^* increases, however, the size of this GYR basin decreases. For $f_A^* \geq \frac{87}{128}$, eventually, the alchemical conversion process catapults the starting, unstable state out of the GYR free-energy basin (which still exists because

FIG. 4: Free energies of GYR and DIA mesostructures as a function of f_A^* at $\chi_{AB}N = 23$. The inset depicts the metastable GYR and DIA mesostructures at $f_A^* = \frac{87}{128}$ as well as the starting, unstable state obtained by the alchemical conversion process. The location of the starting, unstable state on the free-energy landscape is qualitatively sketched.

of the metastable GYR mesostructure) into the DIA free-energy basin. The subsequent, spontaneous structure formation yields the metastable DIA mesostructure.

In summary, we studied the process-directed self-assembly for fabricating metastable mesostructures using dynamic self-consistent field calculations and particle-based simulations. Illustrating the concept by an alchemical conversion process, we have systematically studied the process-accessible mesostructures at intermediate segregation as a function of the initial and final A -volume fractions. In addition to the common equilibrium mesophases, the diagram of process-accessible states encompasses multiple additional mesostructures, of which some have not been reported before. Generally, we find that the sequence of final, metastable mesostructures after the alchemical conversion process coincides in symmetry with the initial, equilibrium mesophase and strongly differs from the equilibrium mesophases at the same value of f_A^* . We argue that this general trend arises from the “weakness” of the alchemical conversion process that does not catapult the starting, unstable state into a new free-energy basin. Notable exceptions are the formation of the metastable DIA and FCC* mesostructures.

Whereas our study focuses on a specific example of a rapid thermodynamic process, we expect that our qualitative observations are rather robust because they are based on the universal structure of the free-energy landscape. We hope that our predictions will stimulate experimental efforts that explore the complex free-energy landscape of these fascinating soft materials, confirm our predictions of novel metastable mesostructures, and test our strategy to reproducibly fabricate the desired metastable

mesostructures.

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 - [52] CPS either refers to face-centered-cubic spheres (FCC) or hexagonally close-packed spheres (HCP).
 - [53] For instance, a spiropyran group can exhibit photo-reversible hydrophilicity change between closed-ring and open-ring forms [21]. Another photo-reversible example is the light-induced *trans* $\rightleftharpoons$ *cis* isomerization of the azobenzene [22] that can significantly change the dipole moment. Additionally, since the alchemical transformation does not need to be photo-reversible, photolabile protecting groups (“cages”) can also be employed to induce light-triggered changes in hydrophilicity, e.g., by photocleavage of NVOC groups [23].
 - [54] The starting, unstable state for $f_A^* < f_A$ can be similarly fabricated by converting an *AAB* copolymer into an *ABB* copolymer.

- [55] Here we only consider process-directed self-assembly that starts from spatially modulated, equilibrium mesophases. One could also start from the disordered phase with thermal fluctuations. The concomitant spinodal self-assembly presumably results often in the formation of the equilibrium mesophases at f_A^* .
- [56] We only consider the FCC arrangement but not the HCP arrangement of close-packed spherical domains.
- [57] The metastable Schoen's F-RD mesostructure can be obtained by joining the enlarged face-centered-cubic A -spheres between the first nearest neighbors. We employ the notations, F-RD and I-WP, according to Ref. [47]
- [58] If we make the connectors in GYR and DIA mesostructures, respectively, become thinner and thinner and finally broken, the spherical domains left result in the formation of GYR-S and DIA-S mesostructures, respectively. We use the notations, I-WP-S, GYR-S, and DIA-S, to label these three metastable spherical mesostructures because the three changes, I-WP-S $\rightleftharpoons$ I-WP, GYR-S $\rightleftharpoons$ GYR, and DIA-S $\rightleftharpoons$ DIA, are all completely gradual.