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¹ The Tricontinuous 3*ths*(5) Phase: A New Morphology in Copolymer ² Melts

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10 Supporting Information

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ABSTRACT: Self-assembly remains the most efficient route to the formation of 11 ordered nanostructures, including the double gyroid network phase in diblock 12 copolymers based on two intergrown network domains. Here we use self-consistent 13 field theory to show that a tricontinuous structure with monoclinic symmetry, 14 called 3ths(5), based on the intergrowth of three distorted ths nets, is an 15 equilibrium phase of triblock star-copolymer melts when an extended molecular 16 core is introduced. The introduction of the core enhances the role of chain 17 stretching by enforcing larger structural length scales, thus destabilizing the 18 hexagonal columnar phase in favor of morphologies with less packing frustration. 19 This study further demonstrates that the introduction of molecular cores is a 2.0 general concept for tuning the relative importance of entropic and enthalpic free 21 energy contributions, hence providing a tool to stabilize an extended repertoire of 22



The cubic gyroid structure^{1,2} of symmetry $Ia\overline{3}d$, with two 24 L intergrown highly symmetric network domains, is a 25 26 ubiquitous complex network phase in soft matter, with a 27 plethora of applications as a functional nanomaterial.³ It forms 28 spontaneously in biological and synthetic systems,² including ²⁹ block copolymers,^{4–7} and is a useful template for metallic and ³⁰ inorganic replicas.⁸ The double gyroid and its chiral single-31 network counterpart of symmetry I4132 (formed e.g. in ³² membrane-templated nanostructures in insects⁹) have demon-³³ strated photonic,^{10,11} plasmonic,^{12,13} mechanical and trans-³⁴ port,¹⁴ electrochromic,¹⁵ or photovoltaic¹⁶ functions, all of 35 which are essentially determined by their network-like 36 morphology. In amphiphilic systems, the gyroid and related 37 network phases form as the result of a delicate balance between 38 interface tension and packing considerations.¹⁷ The interfaces 39 are related to negatively curved triply periodic minimal surfaces, 40 resulting in bicontinuous morphologies with two compartments 41 with network-like topology.

self-assembled nanostructured materials.

The existence of bicontinuous morphologies suggests the 3 possibility of network-like *tricontinuous* structures, based on 44 three intergrown network-like domains. We here consider 45 *balanced* tricontinuous morphologies, where the three domains 46 are of identical shape and their backbones given by the same 47 three-periodic net. The dividing surface between three 48 intergrown nets necessarily contains *triple lines* (shown in 49 yellow in Figures 1 and 3), along which all three network



Figure 1. Candidate morphologies for tricontinuous mesophases with three intergrown network domains. Yellow lines are triple lines, which define the loci of the molecular centers and along which all three domains meet.

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(d) core star triblock (e) dual-chain core star triblock

Figure 2. Different linear and star-copolymer architectures, with and without an extended core.



(c) Interfaces & triple lines (d) Triple lines (top view)

Figure 3. Geometry of the 3*ths*(5) phase. (a) Each component *A*, *B*, and *C* is represented by a distorted monoclinic version of the *ths* net. (b) Three *ths* nets can be intergrown to give the 3ths(5) structure of symmetry group *I*112, with $c/a \approx 4.5-9.5$. (c) Interfaces between the copolymeric components can be illustrated by minimal surface patches that meet along the triple lines which represent the location of the core *X*. (d) The triple lines revolve around straight lines along the crystallographic *c*-axis that are arranged approximately on a triangular lattice.

50 domains meet; the interface is otherwise composed of curved 51 surface patches (modeled as minimal surfaces) between pairs of 52 the three graphs. Numerous tricontinuous structure models 53 have been described.¹⁸⁻²⁵

Tricontinuous morphologies in amphiphilic systems had been proposed theoretically.^{24,26} They became a likely experimental reality with the discovery of the solid IBN-9 mesoporous silicate²⁷ and have very recently been found sexperimentally in gemini surfactants.²⁸ However, the partition of space into a triplet of locally adjacent networks suggests selfassembly via a different molecular architecture, namely from star-shaped molecules with three immiscible arms,²⁹ each arm 61 forming a network-like domain and the molecular cores lying 62 on triple lines. Three-arm molecules have been shown (by 63 simulation^{29–32} and experiment³³) to form a simple hexagonal 64 columnar phase based on the [6.6.6] tiling, referred to here as 65 *hexagonal honeycomb* (unless the molecular structure enforces a 66 spontaneous twist between adjacent molecules¹⁸); cf. Figures 67 f4 4d and 5a. So far, stable balanced tricontinuous phases have not 68 f4 been found in studies of three-arm polyphile molecules in 69 solution,³⁴ or in triblock star-copolymers,³³ or in blends 70 thereof.³⁵

We show here that the introduction of an extended core into 72 the molecular architecture of triblock star-copolymers breaks 73 the free energetic advantage of the columnar hexagonal 74 honeycomb phase, resulting in the tricontinuous phase, termed 75 3ths(5), based on three intergrown 3D nets, labeled *ths* in ref 76 36 (Figure 3). 77

THERMODYNAMIC STABILITY AT INTERMEDIATE 78 SEGREGATION STRENGTHS 79

Spectral self-consistent field theory (SCFT) calculations³⁷ (see 80 also Supporting Information section II) are used to obtain free 81 energy estimates and equilibrium mesophase morphologies,³⁸ 82 for incompressible melts of star-copolymers assuming that the 83 polymeric components are Gaussian chains. The SCFT 84 equations for the density profiles $\rho_K(\vec{r})$ of the copolymeric 85 components *K* are solved in Fourier space by the Anderson 86 mixing scheme³⁹ for a given morphology, providing in 87 particular the free energy *F* and the equilibrium length scale 88 ξ (for which *F* is minimal). Each morphology is encoded as a 89 set of crystallographic basis functions (see Supporting 90 Information section II.C). The equilibrium phase is identified 91 as the morphology which gives the lowest free energy value. 92

We consider the molecular architectures for star-copoly- 93 mers⁴⁰ composed of three polymeric species illustrated in 94 Figure 2. A balanced triblock ABC star-copolymer, henceforth 95 referred to as star-copolymer, consists of three polymeric chains 96 A, B, and C, with equal monomer numbers $N_A = N_B = N_C = N/97$ 3 and with pairwise identical repulsive interaction strength $\chi = 98$ $\chi_{AB} = \chi_{AC} = \chi_{BC}$ per monomer; the chains are covalently linked 99 together at a common junction, the molecular center (Figure 100 2c). A (single-chain) core star-copolymer (Figure 2d) is obtained 101 by replacing the junction with a star-copolymer, called the 102 extended core, with three identical arms of component X. The 103 volume fraction of the core is $f_X = N_X/(N + N_X)$ where N_X is 104 the monomer number of the core. The repulsive interaction 105 strength per monomer between X and the copolymeric chains 106 is $\chi_X = \chi_{AX} = \chi_{BX} = \chi_{CA}$. A dual-chain core star-copolymer (Figure 107 2e) consists of the same core X, where each arm is connected to 108 a pair of A, B, or C chains, each of length N/6.

Our key result is the phase diagram (Figure 4) for dual-chain 110 core star-copolymers which includes significant parameter 111 regions for which the tricontinuous 3ths(5) structure is the 112 stable equilibrium phase. This phase forms at core volume 113 fractions f_X around 20% when the segregation strength χ_X 114 between the core X and the three chains A, B, and C is 115 sufficiently strong. The phase is adjacent to the conventional 116 honeycomb columnar phase³³ at lower core volume fraction f_X 117 or lower segregation ratios χ_X/χ and to another new columnar 118 phase for larger core volumes. Including the polygons 119 representing the core domains, the conventional honeycomb 120 corresponds to the [12.12.3] tiling. For weak segregation of the 121



Figure 4. Phase diagram of dual-chain core star-copolymers for different segregation strengths $\chi N = 40$ (a) and $\chi N = 25$ (b): Data points are results from SCFT simulations, each representing the minimal free-energy phase. See Supporting Information sections II and V for details on the calculation of the phase diagram. (c–e) Representations of the SCFT concentration profiles for the three observed columnar phases; at each point, the color represents the component *K* with the maximal density value $\rho_K(\mathbf{r})$ out of the four components K = A, B, C, and X. Note the deviations of the core regions from a spherical cross section. (c) $\chi N = 40$, $f_X = 0.25$, $\chi_X/\chi = 2$; (d) $\chi N = 40$, $f_X = 0.2$, $\chi_X/\chi = 1.625$; (e) $\chi N = 25$, $f_X = 0.2$, $\chi_X/\chi = 2.36$. See Supporting Information section V for complete representation of phase data. The "disordered" phase is a spatially homogeneous fluid state of all four components (see Supporting Information section II.H).

122 ABC chains ($\chi N \approx 25$, Figure 4b), this novel tricontinuous 123 phase is adjacent to the order-disorder transition.

The 3ths(5) phase is tricontinuous (following the definition of 124 125 ref 18); each of the copolymeric domains A, B, and C forms a single connected (mathematically speaking "continuous") 126 network-like labyrinthine domains, all of identical shape. Each 127 domain is described by a periodic net that is a monoclinic distortion of the *ths* net.³⁶ In common with the nets in the gyroid and O^{70} phases,^{41,42} three edges emanate from each 128 129 130 vertex and the smallest cycles are 10-rings. The 3ths(5)131 132 structure has monoclinic symmetry I112 (space group number in ref 43) with only a single 2-fold axis. The ratio of the 5 133 134 crystallographic lattice parameters is large, around $c/a \approx 4.5-$ 9.5, and the angle between the *a*- and *b*-axes is $\gamma \approx 70^{\circ} - 75^{\circ}$, 135 depending on χN as well as on f_X and χ_X .^{*a*} The fourth 136 component, the core X, forms an infinite array of discrete 137 138 helical rods parallel to the crystallographic c-axis, each 139 representing a triple line.

The phase diagram further contains another new columnar 141 phase, based on the *distorted* [8.8.4] *Archimedean tiling* and of 142 symmetry *cm* (wallpaper group no. 5) (see Figures 4c and 5d). 143 In this phase, the cross sections of the *A*, *B*, and *C* domains are 144 distorted octagons (that in the limit of small cores become 60° 145 rhombi), four of which are arranged around each triple line: 146 two of one material and one of each of the others. In the 147 equilibrium copolymer morphology, the quadrilateral cross sections of the core domains are elongated (Figure 4).^b 148 (Undistorted [8.8.4] tilings, where the cores are not arranged 149 on a triangular lattice, have been observed in copolymeric melts 150 in star-copolymeric melts.^{33,44}) For weaker segregation 151 strengths $\chi N = 25$, an additional columnar phase, termed the 152 *alternating honeycomb*, is found to be stable in a narrow 153 parameter range. However, near the order—disorder transition 154 thermal fluctuations (neglected by the mean-field SCFT 155 theory) are important, making the existence of the alternating 156 honeycomb phase less certain.

The identification of the equilibrium phases rests on 158 comparison of free energies of different test morphologies, 159 computed by spectral SCFT. Our set of test morphologies 160 include the columnar and tricontinuous morphologies detailed 161 in Table 1, lamellar, micellar, and striped lamellar morphologies 162 t1 (see Supporting Information sections II.D, IV, and V). 163

Note that the 3ths(5), the distorted [8.8.4] tiling, and the ¹⁶⁴ alternating honeycomb phase share the common feature that ¹⁶⁵ the triple lines trace lines (straight or slightly curved) ¹⁶⁶ approximately arranged on a triangular lattice. ¹⁶⁷

The key ingredient to the stabilization is the enhanced $_{168}$ entropic chain stretching effect due to introduction of the $_{169}$ extended core X. As the limit of small core volumes in the $_{170}$ phase diagrams shows (see Figure 4 and Supporting $_{171}$ Information section II.G), the $_{3ths}(5)$ phase is not stable $_{172}$ anywhere in the phase diagram of single- or double-chain star- $_{173}$

Table 1. Structural Data and Free Energy Terms for the Candidate Mesophase Morphologies for Star-Copolymer Self-Assembly^a

structure	symmetry	c/a	γ	$A_{ABC}/(LV)^{1/2}$	$L/V\langle z^2 \rangle$
honeycomb	p3m1			1.32	0.192
3cds(1)	P1			1.61	0.179
3ths(109)	$I4_1md$	4.5		1.62	0.174
3ths(5)	I112	4.5	70	1.63	0.167
3 <i>srs</i> (24)	I2 ₁ 2 ₁ 2 ₁			1.78	0.166
3qtz(145)	p3 ₂	1.3		1.89	0.162
alternating honeycomb	p^3			1.86	0.160
6-fold tiling	p^2			2.15	0.160
distorted [8.8.4] tiling	ст			2.15	0.160

^{*a*}Each structure is labeled following the notation of ref 36, with the space group number in parentheses. Where necessary, structural parameters (*c/a* ratio, angles of the unit cell) are chosen as the values corresponding to optimal choices in the numerical SCFT calculations. Note that the data for $\langle z^2 \rangle$ is obtained neglecting the particular curved shape of the interfaces (see Supporting Information section III.A.2). Note the general tendency that an increase in the interface term $A_{ABC}/(LV)^{1/2}$ is accompanied by a lower stretching term $L\langle z^2 \rangle/V$. The family 3ths(109) contains 3 dia(109) as a special case.

174 copolymers without a core. The use of double-chain rather than 175 single-chain core star-copolymers is a further necessary 176 contribution to the stability of this phase. In single-chain core 177 star-copolymers, the 3ths(5) phase is not stable for any value of 178 f_X (see Supporting Information section II.G).

179 An alternative to the use of double-chain core star-180 copolymers that would also likely stabilize the 3ths(5) phase 181 is the use of single-chain core star-copolymers with different 182 statistical segment lengths for the chains that constitute the 183 core and those that constitute the ABC chains. The strong 184 segregation theory suggests this because changing the 185 molecular architecture or the statistical segment lengths alter 186 the stretching free energies (cf. eq 3) in a similar way.

187 THE ROLE OF THE EXTENDED CORE IN 188 EMPHASIZING CHAIN STRETCHING, ELUCIDATED 189 IN THE STRONG SEGREGATION LIMIT

190 The identification of the 3ths(5) structure as a stable 191 tricontinuous phase in star-copolymer melts confirms the 192 intuition gained from the following geometric analysis in the 193 strong segregation limit. In short, the introduction of an 194 extended core into the molecular architecture increases the 195 relative contribution of chain stretching entropy (or packing 196 frustration) relative to interfacial surface tension. This 197 mechanism is sufficient to break the prevalence of the 198 hexagonal columnar honeycomb phase and to tip the balance 199 between interface and chain stretching terms to favor the 200 3ths(5) phase which has less chain stretching frustration but 201 higher surface area than the conventional honeycomb.

The strong segregation theory⁴⁵ (SST) is the limiting case of SCFT, where one considers infinite immiscibility and hence and sharp interfaces between the chemically different components. While SCFT presents the overarching numerical framework applicable to all segregation strengths, the SST allows for the derivation of analytic equations that express the thermodynamic free energy as a function of explicit geometric properties (surface areas, volumes, width homogeneity) of the copolyneric interfaces and domains. In the SST limit, the free energy per copolymer 231

$$\frac{F}{nk_{\rm B}T} = \frac{F_{\rm Int}}{nk_{\rm B}T} + \frac{F_{\rm Conf}}{nk_{\rm B}T} \tag{1}_{212}$$

consists of a surface tension term, $F_{\rm Int}/nk_{\rm B}T = O(1/\xi)$, where ξ 213 is length scale of the structure. The chain stretching term, 214 $F_{\rm Conf}/nk_{\rm B}T = O(\xi^2)$, penalizes configurations that require a high 215 degree of chain stretching in order for the polymeric chains to 216 fill space and fulfill the incompressibility constraint. The surface 217 tension term favors minimal interfacial areas and decreases as 218 $1/\xi$ as the structural length scale ξ increases, hence favoring 219 larger structural lengths, whereas the chain stretching term 220 grows as ξ^2 with ξ , hence favoring smaller length scales. The 221 length scale of the equilibrium structure is the result of 222 minimizing eq 1 with respect to ξ . 223

For the cases of single- and double-chain star-copolymers 224 without a core, the surface tension term reads⁴⁶ 225

$$\frac{F_{\text{Int}}}{nk_{\text{B}}T} = Na\sqrt{\frac{\chi_{AB}}{6}}\frac{A_{ABC}}{V} = O(1/\xi)$$
(2) 226

where A_{ABC} is the combined surface area of all interfaces 227 between distinct species within one unit cell; *V* is the unit cell 228 volume, and *a* is the statistical segment length of each 229 component.

The stretching term reads⁴⁷

$$\frac{F_{\text{Conf}}}{nk_{\text{B}}T} = \sum_{K \in \{A,B,C\}} \frac{3\pi^2}{8f_{K}^2 N a^2 V} \int_{V_{K}} \mathrm{d}^3 r z^2(\vec{r}) = O(\xi^2)$$
(3) 232

where f_K is 1/3 for star-copolymers with three single chains ²³³ (Figure 2c) and 1/6 for the case with pairs of chains.⁴⁸ The ²³⁴ integral in (eq 3) is performed over the regions V_K occupied by ²³⁵ the respective species K. $z(\vec{r})$ can be thought of as the distance ²³⁶ from a point \vec{r} along the shortest coarse-grained polymer path ²³⁷ (in the configuration that minimizes F_{Conf} while obeying the ²³⁸ incompressibility constraint) from the volume element at \vec{r} to ²³⁹ its associated grafting point. While this complex definition of z ²⁴⁰ prevents the exact evaluation of F_{Conf} except for in the simpler ²⁴¹ mesophase morphologies,⁴⁹ approximate expressions discussed ²⁴² below provide estimates for the degree of chain stretching ²⁴³ frustration.

The equilibrium morphology is determined by the 245 minimization of F in eq 1 with respect to different candidate 246 morphologies *and* to the structural length scale ξ (see 247 Supporting Information section III). As stated above, the 248 resulting equilibrium length scale is a compromise between the 249 tendency of the surface tension term to increase ξ and the 250 stretching term to decrease ξ .

Importantly, it turns out³⁸ that this minimization always leads 252 to a length scale ξ such that the ratio $F_{\text{Conf}}/F_{\text{Int}}$ is 253

$$\frac{F_{\text{Conf}}}{F_{\text{Int}}} = \frac{1}{2} \tag{4} _{254}$$

providing the relative weight of the two terms in the 255 equilibrium length scale (see Supporting Information section 256 III.D). 257

For star-copolymers without extended molecular core, the 258 structure minimizing this free energy is the hexagonal columnar 259 phase, a honeycomb structure with triple lines at all hexagon 260 corners (Figure 5a). 261

However, while optimal with respect to interface area, the 262 honeycomb structure has a significant degree of chain 263 stretching frustration. This is best illustrated by the cross- 264



(a) Conventional honeycomb (b) Alternating honeycomb (c) 6-fold tiling (d) Distorted [8.8.4] tiling

Figure 5. Candidate morphologies for columnar phases. Black polygons delineate the spatial regions associated with a given triple line (yellow) and hatched regions the volume domain V_A . The combined cross section of the domains V_A , V_B , and V_C of the conventional honeycomb is a triangle, in contrast to the hexagonal domain cross sections of the alternating honeycomb (b), of the 6-fold tiling (c) and of the distorted [8.8.4] tiling (d). Compared to the triangular shape of the conventional honeycomb, their hexagonal shapes are significantly closer to a segment of a cylinder around the triple line, yielding lower values of $L/V\langle z^2 \rangle$ and hence lower chain stretching. This effect becomes more pronounced for larger cores. Note that the triple line arrangements in (b–d) contain the same triangular lattice.

265 sectional area available to the *A*, *B*, and *C* chains of a star-266 copolymer whose core sits at a triple line: its triangular shape is 267 far from the ideal isotropic (circular) shape with constant 268 radius. Evidently, circular disks do not tile space without gaps 269 and therefore cannot be realized in copolymeric melts. The 270 most nearly circular shape that can form a periodic space-tiling 271 system is the hexagon that results if the triple lines are arranged 272 on a triangular lattice, e.g., in the columnar phases in Figure 273 Sb-d and in approximate form also in the tricontinuous 274 3ths(5) morphology.

This qualitative argument corresponds to the quantitative 275 276 inference that when assuming a fixed triple line length L per unit cell and a fixed unit cell volume V (which together fixes the 277 length scale ξ), the packing term $L/V\langle z^2 \rangle$ is minimal when the 278 domain V_K occupied by copolymer component K = A, B, and C279 is a segment of a cylinder with radial isotropy (see Supporting 2.80 Information sections III.B, III.C, and IV). Any deviation from 281 the cylindrical shape increases $L/V\langle z^2 \rangle$, i.e., the packing 282 frustration. The alternating honeycomb, the 6-fold tiling, and 2.83 the distorted [8.8.4] tiling (Figure 5b–d) have lower stretching 2.84 frustration $L/V\langle z^2 \rangle$ than the conventional honeycomb structure 285 (Table 1). Similarly, the packing frustration of those 286 tricontinuous morphologies whose triple lines follow triangular 287 or other close-packed lattices adopts intermediate values (Table 288 289 1). These considerations clearly emphasize the importance of the arrangement of the triple lines on a close-packed lattice to 290 minimize packing frustration. 291

However, for star-copolymers without an extended core, the small interface term of the conventional honeycomb at the equilibrium length scale outweighs its larger chain stretching frustration.

In order to stabilize the tricontinuous phase (with less stretching frustration but larger interfaces), it is necessary to pronounce the role of the stretching term relative to the surface tension term. This effect is achieved by any mechanism that prevents the system from reducing its structural size: At larger length scales, the contribution of the stretching term to the free energy is larger relative to the surface tension term, thus favoring structures with lower degrees of chain stretching.

304 While the length scale could be constrained explicitly by 305 specific molecular interactions (see Supporting Information

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section III.C.1), we achieve a similar effect by the introduction $_{306}$ of an extended core X. Its primary effect is the creation of $_{307}$ additional interfaces (between A and X, B and X, and C and X) $_{308}$ that increase the surface area. The stretching contribution of $_{309}$ the core star-copolymer is still largely described by eq 3 (see $_{310}$ Supporting Information section III.C.2). The surface tension $_{311}$ term (eq 2) now reads $_{312}$

$$\frac{F_{\text{Int}}}{nk_BT} = Na \left[\sqrt{\frac{\chi_{AB}}{6}} \frac{A_{ABC}}{V} + \sqrt{\frac{\chi_{AX}}{6}} \frac{A_X}{V} \right]$$
(5) 313

where A_X denotes the combined interface area between the 314 core X and K = A, B, and C.^c F_{Int} increases when the volume 315 fraction f_X of the core X or the segregation strength χ_X increase. 316 The resulting equilibrium length scale ξ (at which $F_{int} = 2F_{Conf}$) 317 can become larger when compared to the case without the core. 318 This results in a relatively stronger chain stretching 319 contribution, which in turn stabilizes the tricontinuous 320 3ths(5) phase and the [8.8.4] tiling. 321

While these geometric arguments were developed for the 322 strong segregation regime, the predicted phase sequence of 323 conventional honeycomb, tricontinuous 3ths(5) phase, and 324 [8.8.4] tiling is also observed in the SCFT calculations for 325 intermediate segregation strengths (Figure 4), adding further 326 support to the general validity of this geometric picture. 327

DISCUSSION AND CONCLUSION

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The theoretical analysis of this article now calls for 329 experimental attempts to realize the tricontinuous 3ths(5) 330 phase. Since the purpose of the core is simply the creation of 331 additional interfaces near the triple lines, a variety of 332 realizations are conceivable, e.g., via the introduction of 333 aromatic cores⁵⁰ or nanoparticle–polymer composites.⁵¹The 334 unit cell size can be shielded from shrinkage by e.g. π 335 stacking^{50,52} or H-bonding of cores,^{50,53} thereby also emphasiz- 336 ing the stretching contributions. Maximal stiffness of the core 337 (that suppresses the entropic contributions of the core) and 338 strong interactions χ_X between the core and the other 339 components aid stability. 340

The 3*ths*(5) phase challenges the notion that systems driven 341 toward structural homogeneity—here by virtue of the packing 342 term—tend to adopt highly symmetric morphologies; in soft 343

344 bicontinuous phases this notion has been reinforced through 345 the ubiquity of the cubic bicontinuous phases, where the high 346 symmetry is however a consequence of homogeneity.⁵⁴ The 347 3ths(5) phase, and the O^{70} 41,42 phase of symmetry *Fddd*, 348 demonstrate that packing homogeneity can be achieved without 349 high three-dimensional crystallographic symmetry. On the 350 practical side, the low monoclinic symmetry of the 3ths(5)351 phase with large ratios of the lattice parameters emphasizes the 352 caution that simulation studies in cubic or rectangular simulation boxes fail to observe low-symmetry morphologies. 353 Our results reinforce the role of geometry for the study of 354 355 nanomaterials. Geometric intuition has here provided a 356 shortcut to the design of a fundamentally new nanostructure, 357 bypassing the details of chemical composition or physical interactions and the pitfalls of molecular simulations. Geo-358 359 metric analyses, recognized for the understanding of the $_{360}$ bicontinuous structures, $_{55-58}^{55-58}$ will continue to play a crucial role 361 in converting an ever increasing abundance of possible 362 geometric designs into functional real-world nanomaterials 363 accessible by self-assembly. Where there is matter, there is 364 geometry (Johannes Kepler).

365 ASSOCIATED CONTENT

S Supporting Information 366

367 Self-consistent field theory for block copolymers; spectral 368 method for solving the self-consistent field equations of star-369 copolymers at intermediate segregation; strong segregation 370 theory; geometric analysis of tricontinuous and columnar 371 mesophases; numerical data of all SCFT phase diagrams. This 372 material is available free of charge via the Internet at http:// 373 pubs.acs.org.

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393 **ADDITIONAL NOTES**

^{*a*}The values of c/a and γ vary with χN , f_X and χ_X/χ ; see tables 394 395 in Supporting Information section V. Note that our SCFT 396 analysis does not include an algorithmic free energy 397 minimization with respect to these parameters but rather extracts these values from a coarse manual sampling. 398

399 ^bStrictly speaking, when considering the system as a four-400 component system of A, B, C, and X, the [8.8.4] tiling 401 corresponds to the [8.8.4.8] tiling.

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^cThe interface area A_{ABC} is the interface area between the 402 species A, B, and C, as before. Because of the introduction of $X_{1,403}$ the value of A_{ABC} has however changed. 404

REFERENCES

- (1) Schoen, A. H. Interface Focus 2012, 2, 658-668.
- (2) Hyde, S. T.; O'Keeffe, M.; Proserpio, D. M. Angew. Chem., Int. Ed. 407 2008, 47, 7996-8000. 408
- (3) Bockstaller, M. R.; Mickiewicz, R. A.; Thomas, E. L. Adv. Mater. 409 2005, 17, 1331-1349. 410
- (4) Hajduk, D.; Harper, P.; Gruner, S.; Honeker, C.; Kim, G.; 411 Thomas, E.; Fetters, L. Macromolecules 1994, 27, 4063-4075. 412
- (5) Schulz, M. F.; Bates, F. S.; Almdal, K.; Mortensen, K. Phys. Rev. 413 Lett. 1994, 73, 86-89. 414
- (6) Meuler, A. J.; Hillmyer, M. A.; Bates, F. S. Macromolecules 2009, 415 42, 7221-7250. 416
- (7) Phillips, C. L.; Iacovella, C. R.; Glotzer, S. C. Soft Matter 2010, 6, 417 1693-1703. 418
- (8) Vignolini, S.; Yufa, N. A.; Cunha, P. S.; Guldin, S.; Rushkin, I.; 419 Stefik, M.; Hur, K.; Wiesner, U.; Baumberg, J. J.; Steiner, U. Adv. 420 Mater. 2012, 24, OP23-OP27. 421
- (9) Schröder-Turk, G.; Wickham, S.; Averdunk, H.; Large, M.; 422 Poladian, L.; Brink, F.; Fitz Gerald, J.; Hyde, S. T. J. Struct. Biol. 2011, 423 174. 290-295. 424
- (10) Maldovan, M.; Urbas, A. M.; Yufa, N.; Carter, W. C.; Thomas, 425 E. L. Phys. Rev. B 2002, 65, 165123. 426
- (11) Saba, M.; Thiel, M.; Turner, M. D.; Hyde, S. T.; Gu, M.; 427 Grosse-Brauckmann, K.; Neshev, D. N.; Mecke, K.; Schröder-Turk, G. 428 E. Phys. Rev. Lett. 2011, 106, 103902. 429
- (12) Oh, S. S.; Demetriadou, A.; Wuestner, S.; Hess, O. Adv. Mater. 430 2013. 25. 612-617. 431
- (13) Salvatore, S.; Demetriadou, A.; Vignolini, S.; Oh, S. S.; 432 Wuestner, S.; Yufa, N. A.; Stefik, M.; Wiesner, U.; Baumberg, J. J.; 433
- Hess, O.; Steiner, U. Adv. Mater. 2013, 25, 2713-2716. 434 (14) Torquato, S.; Hyun, S.; Donev, A. Phys. Rev. Lett. 2002, 89, 435
- 266601. 436
- (15) Scherer, M. R. J.; Steiner, U. Nano Lett. 2013, 13, 3005-3010. 437 (16) Crossland, E. J. W.; Kamperman, M.; Nedelcu, M.; Ducati, C.; 438
- Wiesner, U.; Smilgies, D. M.; Toombes, G. E. S.; Hillmyer, M. A.; 439 Ludwigs, S.; Steiner, U.; Snaith, H. J. Nano Lett. 2009, 9, 2807-2812. 440
- (17) Matsen, M.; Bates, F. Macromolecules 1996, 29, 7641-7644. 441 (18) Hyde, S. T.; de Campo, L.; Oguey, C. Soft Matter 2009, 5, 442 443
- 2782 2794
- (19) Elser, V. Philos. Trans. R. Soc., A 1996, 354, 2071-2075. 444 (20) Schoen, A. Infinite Periodic Minimal Surfaces without Self- 445 Intersections; Technical Note TN D-5541, 1970. 446
- (21) Hyde, S. T.; Oguey, C. Eur. Phys. J. B 2000, 16, 613-630. 447
- (22) Hyde, S. T.; Ramsden, S. Europhys. Lett. 2000, 50, 135-141. 448
- (23) Hyde, S. T.; Ramsden, S. J.; Di Matteo, T.; Longdell, J. Solid 449 State Sci. 2003, 5, 35-45. 450
- (24) Hyde, S. T.; Schröder, G. E. Curr. Opin. Colloid Interface Sci. 451 2003, 8, 5-14. 452
- (25) Evans, M. E.; Robins, V.; Hyde, S. T. Acta Crystallogr., Sect. A 453 2013, 69, 241-261. 454
- (26) Schröder-Turk, G. E.; de Campo, L.; Evans, M. E.; Saba, M.; 455 Kapfer, S. C.; Varslot, T.; Grosse-Brauckmann, K.; Ramsden, S.; Hyde, 456
- S. T. Faraday Discuss. 2013, 161, 215-247. 457
- (27) Han, Y.; Zhang, D.; Chng, L. L.; Sun, J.; Zhao, L.; Zou, X.; Ying, 458 J. Y. Nat. Chem. 2009, 1, 123-127. 459
- (28) Sorenson, G. P.; Schmitt, A. K.; Mahanthappa, M. K. Soft Matter 460 2014, 10, 8229-8235. 461
- (29) Kirkensgaard, J. J. K.; Hyde, S. Phys. Chem. Chem. Phys. 2009, 462 11. 2016-2022. 463
- (30) Gemma, T.; Hatano, A.; Dotera, T. Macromolecules 2002, 35, 464 3225-3237. 465
- (31) Tang, P.; Qiu, F.; Zhang, H.; Yang, Y. J. Phys. Chem. B 2004, 466 108, 8434-8438. 467

- 468 (32) Li, W.; Xu, Y.; Zhang, G.; Qiu, F.; Yang, Y.; Shi, A. J. Chem. Phys. 469 **2010**, 133, 064904.
- 470 (33) Matsushita, Y.; Hayashida, K.; Dotera, T.; Takano, A. J. Phys.:
- 471 Condens. Matter **2011**, 23, 284111.
- 472 (34) de Campo, L.; Varslot, T.; Moghaddam, M. J.; Kirkensgaard, J. J.
- 473 K.; Mortensen, K.; Hyde, S. T. Phys. Chem. Chem. Phys. 2011, 13, 474 3139–3152.
- 475 (35) Kirkensgaard, J. J. K.; Evans, M. E.; de Campo, L.; Hyde, S. T.
- 476 Proc. Natl. Acad. Sci. U. S. A. 2014, 111, 1271–1276.
- 477 (36) O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. Acc.478 Chem. Res. 2008, 41, 1782–1789.
- 479 (37) Matsen, M. W.; Schick, M. Phys. Rev. Lett. 1994, 72, 2660-2663.
- 480 (38) Matsen, M. W. J. Phys.: Condens. Matter 2002, 14, R21.
- 481 (39) Matsen, M. Eur. Phys. J. E 2009, 30, 361–369.
- 482 (40) Sioula, S.; Hadjichristidis, N.; Thomas, E. L. *Macromolecules* 483 **1998**, 31, 5272–5277.
- 484 (41) Bailey, T.; Cordell, M.; Epps, T.; Bates, F. *Macromolecules* **2002**, 485 35, 7007–7017.
- 486 (42) Tyler, C. A.; Morse, D. C. Phys. Rev. Lett. 2005, 94, 208302.
- 487 (43) Hahn, T., Ed. International Tables For Crystallography; Kluwer 488 Academic Publishers: Dordrecht, 1992.
- 489 (44) Kirkensgaard, J. J. K.; Pedersen, M. C.; Hyde, S. T. Soft Matter 490 **2014**, *10*, 7182–7194.
- 491 (45) Semenov, A. N. Zh. Eksp. Teor. Fiz. 1985, 88, 1242-1256.
- 492 (46) Helfand, E.; Tagami, Y. J. Chem. Phys. 1972, 56, 3592-3601.
- 493 (47) Likhtman, A. E.; Semenov, A. N. *Macromolecules* **1994**, 27, 494 3103–3106.
- 495 (48) Milner, S. T. Macromolecules 1994, 27, 2333-2335.
- 496 (49) Likhtman, A. E.; Semenov, A. N. *Macromolecules* **1997**, *30*, 497 7273–7278.
- 498 (50) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.;
- 499 Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, 500 M. Angew. Chem., Int. Ed. **2007**, 46, 4832–4887.
- 501 (51) Warren, S. C.; Messina, L. C.; Slaughter, L. S.; Kamperman, M.;
- 502 Zhou, Q.; Gruner, S. M.; DiSalvo, F. J.; Wiesner, U. *Science* **2008**, *320*, 503 1748–1752.
- 504 (52) Pisula, W.; Feng, X.; Müllen, K. *Adv. Mater.* **2010**, *22*, 3634– 505 3649.
- 506 (53) Paraschiv, I.; de Lange, K.; Giesbers, M.; van Lagen, B.;
- 507 Grozema, F. C.; Abellon, R. D.; Siebbeles, L. D. A.; Sudholter, E. J. R.;
- 508 Zuilhof, H.; Marcelis, A. T. M. J. Mater. Chem. 2008, 18, 5475-5481.
- 509 (54) Schröder-Turk, G. E.; Fogden, A.; Hyde, S. T. *Eur. Phys. J. B* 510 **2006**, *54*, 509–524.
- 511 (55) Hyde, S. T.; Andersson, S.; Larsson, K.; Blum, Z.; Landh, T.;
- 512 Lidin, S.; Ninham, B. *The Language of Shape*; Elsevier Science: 513 Amsterdam, 1997.
- 514 (56) Scriven, L. Nature 1976, 263, 123-125.
- 515 (57) Thomas Edwin, L.; Anderson David, M.; Henkee Chris, S.; 516 Hoffman, D. *Nature* **1988**, 334, 598–601.
- 517 (58) Andersson, S.; Hyde, S. T.; Larsson, K.; Lidin, S. *Chem. Rev.* 518 **1988**, 88, 221–242.