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PAPER

The diamond and other non-conventional morphologies in two-scale multiblock AB copolymers†

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We revisit the idea of the existence of the ordered block copolymer phase possessing diamond symmetry $Fd\bar{3}m$ (space group No. 227), which was first put forward within the framework of the strong segregation approach. For this purpose we study the order–disorder and order–order transitions in molten two-scale multiblock copolymers $A_{mN/2}(B_{N/2}A_{N/2})_nB_{mN/2}$ via the pseudo-spectral numerical procedure of the self-consistent field theory (SCFT). The phase diagram in the plane $(f_C, \tilde{\chi})$, where $f_C = n/(m+n)$ and $\tilde{\chi} = \chi N(m+n)$ is the effective energetic Flory–Huggins parameter, is built and some accompanying quantities are analyzed. Near the order–disorder transition line the phase diagram contains the regions where the lamellar, alternating gyroid, diamond and simple cubic phase, respectively, exist. With an increase of the degree of segregation, the diamond phase is replaced by a tetragonal array of cylinders (simple square) phase, which agrees with the preceding results obtained within the Leibler-like weak segregation theory, and with the SCFT calculations for a physically similar melt of linear ABC triblock copolymers with a non-selective middle block. Thus, the diamond morphology in the system under study is shown to exist as an essentially weak or moderately (not strongly) segregated phase. The ways to visualize the patterns of ordering in such morphologies are discussed. A new quantity (topological permeability) to characterize the transport properties in 3D bicontinuous morphologies is introduced and first calculated for real block copolymer ordered morphologies. Some implications of the results obtained for the design of the block copolymer thin films with improved permeability are discussed.

1. Introduction

The diamond morphology possessing the symmetry $Fd\bar{3}m$ (space group No. 227) was first suggested to exist in ordered block copolymer melts by Hashimoto *et al.*^{1,2} When studying polystyrene–polyisoprene (PS–PI) diblock copolymers within the interval $0.66 \geq \phi_{PS} \geq 0.62$, where ϕ_{PS} is the polystyrene volume fraction, they observed a characteristic pattern on some TEM micrographs (see Fig. 1), which the authors interpreted as evidence of an ordered structure comprised of some tetrapod units. Based on crystallographic considerations, the authors found the corresponding morphologies to be i) a *diamond* the authors called a *single diamond* (D), ii) a *double diamond* (DD), and iii) a *wurtzite* lattice. Finally, Hashimoto *et al.*¹ concluded that the most probable morphology to fit their data is a DD $Pn\bar{3}m$ (space group No. 224) that has only been reported by

Thomas *et al.*³ to be found in the PS–PI star block copolymers. The DD phase has also been reported to appear in the linear ternary poly(isoprene-*b*-styrene-*b*-2-vinylpyridine) block copolymers,^{4–6} this finding was supported *via* a theoretical study⁷ based on a mix of the strong segregation theory (SST) and some phenomenological considerations.⁸

Fig. 1 TEM micrograph of the PS–PI (with the total molecular weight $M_n = 186\,000$ and PS volume fraction $\phi_{PS} = 0.66$) film cast from solution in toluene. A tetrapod unit is marked by the circle and the arms perpendicular to the section surface are marked by arrows (reprinted with permission from ref. 2).

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† Diamond morphology in multiblock copolymers.

The next development was a dramatic page in the history of block copolymer physics. First, the experimental data were re-interpreted as evidence for the *double gyroid Ia $\bar{3}d$* (space group No. 230) or *alternated gyroid I4 $\bar{1}32$* (space group No. 214) morphologies rather than the *double diamond one* (see ref. 9–12 and numerous cited and related papers). Next, theoretical considerations carried out within the strong segregation theory (SST),^{13–15} weak segregation theory (WST)¹⁶ and self-consistent field theory (SCFT) numerical procedure¹² failed to prove that the DD phase could be the most thermodynamically stable equilibrium phase for star (in particular, diblock) AB copolymers at any composition and ternary ABC block copolymers. Accordingly, interest in the diamond phases has been lost for a decade.

Another line of development was initiated within the WST in the seminal paper by Leibler¹⁷ who first described a non-conventional phase he found to be metastable only in diblock copolymers and called, due to reasons we describe below, the face-centered cubic (FCC) phase. Later the phase has been shown to become stable within the WST, firstly for some phenomenological Hamiltonians^{18,19} and secondly in the ternary ABC triblock copolymer melts²⁰ with a middle block that is non-selective with respect to the end blocks (see Fig. 2a). This class of ternary ABC copolymers comprises the well-studied poly(isoprene-*b*-styrene-*b*-2-vinylpyridine)^{4–6} and poly(isoprene-*b*-styrene-*b*-ethyleneoxide)^{21,22} block copolymers. Finally, it was realized recently²³ that the presumable FCC is, in fact, the D phase. Moreover, Qin *et al.*²³ showed, *via* the SCFT, that the D phase stability regions in ABC block copolymers extends from weak to moderate segregation realm and disappears with an increase of the segregation degree. Thus, the D phase, first expected to exist in block copolymers within the strong segregation paradigm² unexpectedly turned out to be essentially a weakly (or, at most, moderately) segregated phase.

One more interesting system where the diamond phase is expected to exist is related to the so-called two-scale multiblock AB copolymers $A_{f m N/2}(B_{N/2}A_{N/2})_n B_{(1-f) m N/2}$ first studied by Nap *et al.*²⁴ for $f = 0$ as a theoretical model to analyze the *structure-in-structure* mesophases that were found earlier experimentally.²⁵ Symmetric undecablock polystyrene–polyisoprene copolymers SISISISIS (S-*b*[(I-*b*-S)₄-*b*-I]-*b*-S) with two long polystyrene (S) end blocks and comparatively short blocks of polystyrene and polyisoprene forming the middle multiblock were first synthesized by Matsushita *et al.*²⁶ *via* anionic polymerization and these revealed a clear two-scale *lamellar-in-lamellar* structure.²⁶ On the other hand, it was theoretically argued within the WST^{27,28} and verified *via* the SCFT²⁹ that the antisymmetric two-scale multiblock copolymers $A_{m N/2}(B_{N/2}A_{N/2})_n B_{m N/2}$ would mimic the ABC ternary copolymers (see Fig. 2b) with the proper composition not too far away from the order–disorder transition (ODT) line whereas for higher segregation these antisymmetric two-scale multiblock copolymers are expected to reveal the

Fig. 2 The architectures of the block copolymers expected to reveal the diamond morphology: a) ternary ABC block copolymers; b) binary two-scale multiblock copolymers $A_{m N/2}(B_{N/2}A_{N/2})_n B_{m N/2}$.

lamellar-in-lamellar mesophases.³⁰ Indeed, within our own group, (G, tB) two-scale multiblock copolymers of polystyrene and poly(*p*-hydroxy-styrene) were prepared through sequential anionic polymerization of styrene and *tert*-butoxy-styrene (tBOS) followed by hydrolysis of the *tert*-butoxy group. A hexablock (S-*b*[(HS-*b*-S)₂]-*b*-HS) and an octablock (S-*b*[(HS-*b*-S)₃]-HS) were prepared. In the latter a lamellar-in-lamellar morphology with two “thin” S and HS layers in between a thick S and a thick HS layer were observed³¹ in accordance with the SCFT consideration.

The purpose of the present paper is to check whether the D phase in antisymmetric two-scale multiblock copolymers shown in Fig. 2b could also be observed as a weakly or, perhaps, moderately segregated phase not affected by the structure-in-structure formation and study, *via* the SCFT, the stability and properties of the diamond phase. As a bonus, we compared the results we obtained with those presented in ref. 23 for the ABC copolymers that provide an important insight into the effects caused by the composition heterogeneities (*cf.* Fig. 2a and 2b). The presentation of this paper is as follows. In section 2 we discuss in detail the general symmetry properties of the FCC and D phase and the corresponding extinction rules. As a result, we provide proof of the fact that the weakly segregated phase first considered by Leibler¹⁷ and misleadingly referred to by him (and also by us^{19,20,28,29}) as the FCC phase is, in fact, the D phase. In section 3 the model and the calculation procedure are briefly described. The results (the phase diagram, temperature dependence of the ordered phases period and that of Fourier spectrum of the order parameter) and their discussion are presented in section 4. Some conclusions are given in section 5.

2. The diamond phase: visualization, symmetry, extinction rules and WST description

Atomistic and order parameter visualizations

The diamond phase (space group No. 227) is a crystal phase whose symmetry is that of a complex cubic phase with eight atoms in the primitive cubic cell with edge L shown in Fig. 3, *i.e.*

Fig. 3 The primitive cell of the diamond phase. Eight atoms are located at the cube vertices, six atoms are located at the centers of the cube faces and four atoms, which are obtained *via* shifting of one of the vertex atoms and three of the face atoms by 1/4th of the diagonal inside the primitive cubic cell.

it is comprised of two face-centered cubic lattices, one of which is shifted with respect to the other by 1/4th of the diagonal of the primitive cubic cell.

The atomistic visualization described is often used to get an idea of the diamond lattice symmetry for simple solid species comprised of particles, which are basically fixed at the nodes of the corresponding crystal lattice. The situation is rather different in the ordered block copolymer systems where the lattice period is much bigger than the characteristic distance between the neighboring particles. In that case separate particles are moving almost freely within the whole lattice cell so that it is only the collective density distribution functions $\rho_i(\mathbf{r})$ of the particles (where i labels the sort of the particles) that possess the crystal symmetry properties. A good tool to get an idea of these crystal symmetry properties is provided by plotting so-called order parameter level surfaces³² (OPLS) defined as follows:

$$\Psi_i(\mathbf{r}) = \rho_i(\mathbf{r}) - \bar{\rho}_i = c. \quad (1)$$

Here the functions $\Psi_i(\mathbf{r})$ are called order parameter, $\bar{\rho}_i$ is the average (over the whole volume of the system) value of the number density of the particles of the i -th sort and c is the level value. If $c = 0$ then the surface (1) divides the system into regions with an excess and a lack of the i -th component. For incompressible binary AB block copolymers the OPLS with various symmetries and $c = 0$ were discussed in ref. 33 and called inter-material dividing surfaces (IMDS). The OPLS with $c > 0$ ($c < 0$) delineate the region with a finite (and high enough) excess (lack) of the component of the i -th sort that determines the mechanical and transport properties of the arising nanostructures and might be observed *via* TEM micrographs made with a selective to component i staining agent.

OPLS, minimal surfaces and quasi-atomistic visualization

It is known³³ that the OPLS with $c = 0$ are a good approximation of so-called triply periodic minimal surfaces with the same symmetry. For example, within the weak segregation approximation we discuss below the zero level OPLS for the simple cubic lattice reads

$$\Psi(\mathbf{r}) = \cos(2\pi x/L) + \cos(2\pi y/L) + \cos(2\pi z/L) = 0. \quad (2)$$

The surface looks very similar to the Schwarz's P-surface³³ as is seen from Fig. 4a. On the other hand, the OPLS (1)–(2) with $c_{\text{e} \rightarrow +0} \rightarrow 3 - \varepsilon$ or $c_{\text{e} \rightarrow +0} \rightarrow -3 + \varepsilon$ reproduce the atomistic visualization well. The corresponding surfaces shown in Fig. 4b and 4c could be referred to as the *quasi-atomistic visualization*. It is tempting to ask which of the cases provides a better physical idea of the morphology under discussion but such a question is incorrect. It is seen by tracing the order parameter profile^{29,30} in weakly and moderately segregated block copolymers that there is only a rather smooth intermediate layer between the different domains, which by no means can be treated as a real interface.† Thus, it is only the full 3D order parameter profile $\Psi(\mathbf{r})$

† A strong assertion worth of discussion, which follows from this fact, is that the fruitfulness of the notion of minimal (constant mean curvature) surfaces in the field of block copolymer nanostructures is strongly overestimated.

that provides an adequate description of the ordered block copolymer (generally, an ordered soft matter) morphology. A good 2D representation of such a 3D profile gives an animation of the morphologies *via* a series of the OPLS with a running value of c .

OPLS and Percolation properties

Considering that the OPLS families is a good route to study the transport processes through the triply periodic morphologies, which are determined by the connectivity of the corresponding OPLS, we considered the OPLS family for the normalized order parameter

$$\bar{\Psi}(\mathbf{r}) = \Psi(\mathbf{r})/(\max \Psi(\mathbf{r})) = c. \quad (3)$$

The topology of the surfaces is determined by both the value of c and the character of the order parameter profile. Let $\Psi(\mathbf{r})$ be defined by expression (2). The corresponding OPLS are presented in Fig. 5. We see that for $|c| < q = 0.33$ the OPLS is a 1-connected surface, which extends over the whole infinite volume of the system and looks like a set of islands connected by thin channels (see Fig. 5a, b). At $c = q$ the channels vanish (see Fig. 5c) and for $|c| > q$ the OPLS is decomposed into many finite disconnected surfaces, each of which could be placed inside the corresponding elementary cell (see Fig. 5d, e); the number of these finite surfaces is determined by the morphology symmetry whereas their total volume per elementary cell decreases with increase of c until it vanishes at $c = 1$.

Remarkably, the value of the connectivity threshold q depends considerably on both the symmetry and the whole profile of the order parameter. For example, for the FCC and diamond morphologies we discuss below the WST values of q are $q_{\text{FCC}} = 0$ and $q_{\text{D}} = 0.7$. This means that when a probe particle can penetrate through a substance only along those regions where the concentration of one (affine) component is high enough, the percolation cluster of the high-concentration channels would never appear in the FCC and it would appear earlier in the D phase rather than in the SC one. This fact enables us to call c_1 the topological permeability since it gives a good qualitative idea to compare the transport properties of various morphologies (see below).

Extinction and phase shift rules

To find the most representative expressions for the OPLS (1) of different crystal symmetries one has to establish certain relationships, which are imposed by the very symmetry of the morphology and hold for the amplitudes $A_{\mathbf{q}}$ appearing in the Fourier series for the order parameter

$$\Psi(\mathbf{r}) = \sum_{\mathbf{q}} A_{\mathbf{q}} \exp(i\mathbf{q}\mathbf{r}) \quad (4)$$

with the vectors $\mathbf{q}$ running all the nodes of the reciprocal simple cubic lattice:

$$\mathbf{q} = 2\pi(\mathbf{i}l + \mathbf{j}m + \mathbf{k}n)/L \quad (5)$$

where $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are the unit vectors directed along the basic edges of the cubic cell, and l, m, n are the integers.

Fig. 4 The OPLS visualization of the weakly segregated simple cubic morphology. a) Zero level OPS approximating the minimal Schwarz's P-surface; b) and c) the quasi-atomistic OPLS with $c = -0.45$ and $c = 0.45$, respectively.

Now, if $\Psi_{\text{sc}}(\mathbf{r})$ is an arbitrary spatial distribution of the order parameter satisfying a simple cubic lattice symmetry, then, generally, the amplitudes appearing in the series (4) will differ from zero for any triple of the integers (l, m, n) :

$$A_{\mathbf{q}}^{\text{sc}} = \int_0^L \int_0^L \int_0^L \Psi_{\text{sc}}(\mathbf{r}) \exp(-i\mathbf{q}\mathbf{r}) \, dx \, dy \, dz \neq 0 \quad (6)$$

for any integer triple (l, m, n)

However, assertion (6) does not hold for complex lattices like the FCC lattice *etc.* Indeed, due to its very symmetry, an arbitrary spatial distribution of the order parameter corresponding to the FCC lattice reads

$$\Psi_{\text{fcc}}(\mathbf{r}) = \Psi_{\text{sc}}(\mathbf{r}) + \Psi_{\text{sc}}(\mathbf{r} + \mathbf{a}_1) + \Psi_{\text{sc}}(\mathbf{r} + \mathbf{a}_2) + \Psi_{\text{sc}}(\mathbf{r} + \mathbf{a}_3) \quad (7)$$

with $\mathbf{a}_1 = L(\mathbf{i} + \mathbf{j})/2$, $\mathbf{a}_2 = L(\mathbf{j} + \mathbf{k})/2$, $\mathbf{a}_3 = L(\mathbf{i} + \mathbf{k})/2$. Thus, the amplitudes appearing in the series (4) for the FCC lattice read

$$A_{\mathbf{q}}^{\text{fcc}} = A_{\mathbf{q}}^{\text{sc}} \left(1 + (-1)^{l+m} + (-1)^{m+n} + (-1)^{l+n} \right) = \begin{cases} 4A_{\mathbf{q}}^{\text{sc}} & \text{all } (l, m, n) \text{ are odd} \\ 4A_{\mathbf{q}}^{\text{sc}} & \text{all } (l, m, n) \text{ are even} \\ 0 & (l, m, n) \text{ are of different parity} \end{cases} \quad (8)$$

Eqn (8) is a particular case of so called extinctions rules³⁴ (the relationships specifying which of the Fourier harmonics appearing in the series (4) vanish identically due to the very symmetry of the lattice under consideration). Similarly, for the diamond phase we have

$$\Psi_{\text{diamond}}(\mathbf{r}) = \Psi_{\text{fcc}}(\mathbf{r} - \mathbf{b}) + \Psi_{\text{fcc}}(\mathbf{r} + \mathbf{b}) \quad (9)$$

with $\mathbf{b} = L(\mathbf{i} + \mathbf{j} + \mathbf{k})/8$ and, therefore, the desired extinction rules read

$$A_{\mathbf{q}}^{\text{diamond}} = 2A_{\mathbf{q}}^{\text{fcc}} \cos((l + m + n)\pi/4) = \begin{cases} 2A_{\mathbf{q}}^{\text{fcc}}(-1)^k & l + m + n = 4k \\ 0 & l + m + n = 4k + 2 \\ \sqrt{2}A_{\mathbf{q}}^{\text{fcc}}(-1)^k & l + m + n = 4k \pm 1 \end{cases} \quad (10)$$

It is worth noting that the extinction rules (10) not only prescribe complete vanishing of the diamond harmonics with $l + m + n = 4k + 2$, but also impose alternating of the amplitudes sign (as compared to that in the simple cubic lattice) with a change of the value of the sum $l + m + n$. Indeed, it follows from eqn (8) and (10) that in the weak segregation limit, when the Fourier series (4) comprises the harmonics belonging to the 1st coordination

Fig. 5 To the definition of the topological permeability. The 1-connected OPLS at $c = 0$ (a) and $c = 0.3$ (b), the boundary (as to vanishing of the percolating cluster) OPLS at $c = c_1 = 0.33$ (c) and disconnected OPLS at $c = 0.36 > c_1$ (d) and $c = 0.9 > c_1$.

sphere ($l, m, n = \pm 1$) only, the expressions for the order parameter with the FCC and D symmetries, respectively, read

$$\Psi(\mathbf{r}) = A(\cos(\bar{q}(x + y - z)) + \cos(\bar{q}(y + z - x)) + \cos(\bar{q}(x + z - y)) + \cos(\bar{q}(x + y + z))) \quad (11a)$$

and

$$\Psi(\mathbf{r}) = A(\cos(\bar{q}(x + y - z)) + \cos(\bar{q}(y + z - x)) + \cos(\bar{q}(x + z - y)) - \cos(\bar{q}(x + y + z))) \quad (11b)$$

with $\bar{q} = 2\pi/L$.

As will be shown below, the difference in the last addendums in eqn (11a) and (11b) is crucial in many physical aspects. But first we notice that both 11a and 11b can be written in the form

$$\Psi(\mathbf{r}) = A \sum_{k=1}^4 \cos(\mathbf{q}_k \mathbf{r} + \Omega_k), \quad (12)$$

where

$$\begin{aligned} \mathbf{q}_1 &= q^*(1, 1, -1)/\sqrt{3}, & \mathbf{q}_2 &= q^*(1, -1, 1)/\sqrt{3}, \\ \mathbf{q}_3 &= q^*(-1, 1, 1)/\sqrt{3}, & \mathbf{q}_4 &= -q^*(1, 1, 1)/\sqrt{3} \end{aligned} \quad (13)$$

with $q^* = \sqrt{3}\bar{q} = 2\pi\sqrt{3}/L$ and $\Omega_i = 0$, $i = 1, 2, 3$ whereas $\Omega_4 = 0$ and $\Omega_4 = \pi$ for the FCC and D phases, respectively. Thus, the only difference between the FCC and D phases within the 1st coordination sphere order parameter descriptions in (11) and (12) is the presence of the phase shift by π for one of the first harmonics. Nevertheless, this difference alone leads to radical morphological changes as shown in Fig. 6 and 7.

More precisely, the only infinite (percolating) OPLS for the FCC morphology is that with $c = 0$, whereas the OPLS delineating the regions with a finite excess of, say, the component of the i -th sort are separated into non-overlapping islands as shown in Fig. 6. Thus, the topological permeability is $q = 0$ for the FCC. On the contrary, for the D morphology the regions with a finite excess of one of the components form some infinite triply periodic clusters as is seen from Fig. 7. One can check that for the weak segregated diamond morphology, the topological permeability $q \approx 0.7$.

3. The model and method

Model

We systematically studied the formation of morphologies for the specified class of systems with a two-length-scale architecture denoted as $A_{mN/2}(B_{N/2}A_{N/2})_nB_{mN/2}$, shown in Fig. 2b. These linear chains consist of two long A and B end blocks connected

by a sequence of n repeating symmetric diblocks $B_{N/2}A_{N/2}$. N , nN , $mN/2$, and $N_{\text{tot}} = (m + n)N$ are the degrees of polymerization of the elementary repeated diblock, the middle multiblock part, the tails and the whole chain, respectively. All blocks are supposed to be flexible. For simplicity, the statistical segment lengths a and excluded volumes v_0 are supposed to be the same both for A and B monomers.

Weak segregation theory (WST)

An insight into the nature of the morphologies formed in such a system can be gained from the WST consideration based on the Landau expansion for the free energy

$$\begin{aligned} \frac{\Delta F}{T} &= \frac{1}{2} \int \Gamma_2(q) \psi(\mathbf{q}) \bar{\psi}(\mathbf{q}) \frac{d\mathbf{q}}{(2\pi)^3} \\ &+ \sum_{n=3}^4 \frac{1}{n!} \int \Gamma_n(\mathbf{r}_1, \dots, \mathbf{r}_n) \prod_{a=1}^n \psi(\mathbf{r}_a) d\mathbf{r}_a \end{aligned} \quad (14)$$

where

$$\Psi(\mathbf{r}) = \frac{(\phi_B(\mathbf{r}) - \bar{\phi}_B) - (\phi_A(\mathbf{r}) - \bar{\phi}_A)}{2} = \frac{\phi_B(\mathbf{r}) - \phi_A(\mathbf{r})}{2} \quad (15)$$

is the order parameter and $\psi(\mathbf{q}) = \int \Psi(\mathbf{r}) \exp(i \mathbf{q} \mathbf{r}) d\mathbf{r}$, $\phi_A(\mathbf{r})$ and $\bar{\phi}_i$ are, respectively, the local and volume averaged values of the volume fractions of the repeated units (monomers) of the sort i ($i = A, B$) and the vertices Γ_n can be explicitly related to the flexible block copolymer architecture as first shown by Leibler for molten diblock copolymers in his seminal paper¹⁷ (for some peculiarities of the WST application to more complicated block copolymers see ref. 20,27,28,35,36). In particular,

$$\Gamma_2(q) = (N_{\text{tot}} \tilde{g}(m, n, Q^2))^{-1} - 2\chi, \quad (16)$$

where $Q = \sqrt{q^2 a^2 N_{\text{tot}}/6}$ is the reduced wave vector, the quantity $\tilde{g}(m, n, Q^2)$ calculated as a function of Q in ref. 23,24, has a maximum at $Q = Q^* > 0$ and χ is the conventional Flory–Huggins parameter.^{37,38}

Due to the symmetry under the $A \leftrightarrow B$ exchange of the copolymer architecture, when under observation the cubic (in powers of Ψ) term in eqn (13) vanishes.^{27,28} Therefore, for $\tau = 2$ ($\tilde{\chi}_c - \tilde{\chi}) > 0$, where

$$2 \tilde{\chi}_c = \min \tilde{g}^{-1}(m, n, Q^2) = \tilde{g}^{-1}(m, n, Q_*^2), \quad \tilde{\chi} = N_{\text{tot}} \chi, \quad (17)$$

both the minimal value of the free energy (14) and the corresponding order parameter (15) are equal to zero, whereas for $\tau < 0$ the minimal value of the free energy is negative and the corresponding order parameter is a finite function expandable in

Fig. 6 The OPLS for the FCC symmetry with the (properly normalized) order parameter (11a). The zero-level OPS (IMDS) is shown left, the OPLS with finite negative and positive values of c are shown, respectively, in the middle and right. Neither of the OPLS but IMDS is 1-connected.

Fig. 7 The OPLS for the D symmetry with the (properly normalized) order parameter (11b). a) and e) the disconnected (quasi-atomistic) OPLS at $c = -0.74$ and $c = 0.74$, respectively; b)–d) the 1-connected OPLS at $c = -0.68$, $c = 0$ and $c = -0.68$, respectively. The boundary OPLS corresponding to $|c| = c_1 = 0.7$ are not shown.

the Fourier series (4). In other words, the point $\tau = 0$ is the order–disorder transition (ODT) point.

In the vicinity of the ODT ($\tau < 0$, $|\tau| \ll 1$) the weak segregation holds and the series (4) is supposed to include the harmonics belonging to the only dominant coordination sphere (typically, the first one):

$$\Psi_{\text{WST}}(\mathbf{r}) = A \sum_{|\mathbf{q}_i|=q^*} \exp(i(\mathbf{q}_i \mathbf{r} + \alpha(\mathbf{q}_i))) \quad (18)$$

where q^* is the radius of the 1st coordination sphere, $\alpha(-\mathbf{q}_i) = -\alpha(\mathbf{q}_i)$ and the amplitude A and free energy ΔF read

$$A^2 = -\tau/\beta_{\mathfrak{H}}, \quad \Delta F/T = -\tau^2/(2\beta_{\mathfrak{H}}), \quad (19)$$

where $\beta_{\mathfrak{H}}$ is a coefficient, which depends both on the multiblock copolymer architecture (*via* the vertex Γ_4 appearing in eqn (14)) and the symmetry of the reciprocal lattice $\mathfrak{H}$ under consideration.

Thus, the order–disorder transition in the system is a continuous 2nd order phase transition from the disordered phase to an ordered phase whose symmetry is determined by the details of the multiblock architecture. More precisely, the corresponding WST calculations^{27,28} of the coefficient $\beta_{\mathfrak{H}}$ show that the morphology of the arising ordered phase is determined by the reduced tail length m and the number n of the repeated diblocks $B_{N/2}A_{N/2}$ according to the phase portrait presented in Fig. 8. Therewith, the succession of the morphologies replacing each other with an increase of m depends on the value of n . As seen from Fig. 8 these successions could be LAM₁–alternating gyroid (G^A)–LAM₂ or LAM₁– G^A –D– G^A –LAM₂ or LAM₁–simple cubic (SC)–D– G^A –LAM₂ or LAM₁–body-centered cubic (BCC)–SC–D– G^A –LAM₂. The most characteristic for the two-scale multiblock copolymers is the appearance of the small-scale lamellae LAM₁ and large-scale lamellae LAM₂, which is due to the fact that when the tails are comparatively small then the morphology is basically determined by the scale of the short blocks forming the middle multiblock part, the incompatibility parameter governing

the segregation degree being $\bar{\chi} = \chi N$. On the contrary, when the tails are of the scale or even bigger than the whole middle multiblock part, then the morphology scale is that of the whole chain. In the latter (large-scale) case the phase behavior is similar to that of the symmetric ABC block copolymers,²⁰ the incompatibility parameter governing the degree of such large-scale segregation being $\tilde{\chi} = \chi N_{\text{tot}} = (m + n)\bar{\chi}$. In that case large-scale microphase separation starts at $\tilde{\chi} > \tilde{\chi}_c \sim 10$ whereas structure-in-structure formation starts³⁰ at $\bar{\chi} > \bar{\chi}_c \sim 10$. If both m and n are of the order of the unity then, obviously, one can not distinguish the large- and small-scale types of morphologies anymore. For more detail including the rigorous distinction between the LAM₁ and LAM₂ morphologies see ref. 27 and 28.

Summarizing, if the middle part of a block copolymer is effectively non-selective with respect to the tails, then the conventional lamellar phase is expected to be replaced by various cubic phases when the relative length of the tails decreases.

A hand-waving argument to explain this general architecture effect is that the entropic loss due to the chain confinement into

Fig. 8 The phase portrait in the plane (n, m) for the symmetric two-scale multiblock copolymers indicating the architectures providing stability of lamellar and various cubic phases (left). The enhanced image of the fine structure of the phase portrait within the dotted rectangle is shown in the right picture.

parallel layers (lamellar morphology) is bigger than that into domains characteristic for morphologies of a cubic symmetry.

Self-consistent field theory (SCFT)

Expressions (14) for the free energy of block copolymer melts with a non-uniform composition and (18) for the order parameter can be viewed as those obtained by neglecting the higher terms in powers of Ψ in the actual non-polynomial expression for the free energy and higher harmonics in the full Fourier series (4). The procedure to calculate such a genuine free energy has been elaborated within so called SCFT.^{39–41} To study the two-scale multiblock copolymers under consideration beyond the WST description we solve numerically the SCFT equations^{39–41} using the pseudospectral approach^{42,43} and the Ng⁴⁴ iterative procedure. To speed up the calculations the initial guesses for the iterative procedure are chosen based on the information on the plausible morphologies provided by the WST. There is no need to present here a more lengthy description of the SCFT procedure, which is already given in ref. 29,30 and 39–41.

4. Results and discussion

Phase diagrams

To begin with, let us look at the phase behavior of ABC triblock copolymers shown in Fig. 2a. The corresponding phase diagram built *via* the SCFT²³ is presented in Fig. 9a. It is very similar to the WST prediction²⁰ apart from two distinctions. The first, a minor one, is that the simple cubic phase (space group $Pm\bar{3}m$) is referred to by the authors²³ as S^A (alternating spheres) or even alternating BCC. In this way the authors²³ emphasize the fact that the quasi-atomistic visualization *via* the OPLS possessing the simple cubic symmetry described in Section 2 could be interpreted as an image of two alternating lattices of minima (Fig. 4b) and maxima (Fig. 4c), which form together a CsCl type cubic lattice. The second (and quite substantial) distinction is that beyond the WST validity realm when the side blocks become

more incompatible the diamond phase is found to undergo the 1st order phase transition into a phase of “alternating” cylinders, which is just a plane counterpart of the S^A (SC) phase.

Our target was to check what is the influence of the inner structure of the middle block on the general outline of the phase diagram and, especially, whether the *structure-in-structure* formation would not appear before the D- S^A transition. For this purpose we calculated *via* SCFT the free energies and accompanying quantities for the trial morphologies LAM, D, G^A , C^A and S^A and found the most thermodynamically stable morphology at each point $(f_C, \tilde{\chi})$, where $f_C = n/(m+n)$ is the average volume fraction of the middle multiblock part of the copolymer (for definiteness, we fix the value of $n = 6$). The phase transition lines where two of the prescribed morphologies simultaneously have the same minimal free energy are plotted in the corresponding phase diagram (see Fig. 9b).

As seen from Fig. 9, the phase diagrams for the ternary ABC and binary AB two-scale multiblock copolymers with an effectively non-selective middle block are very similar. More precisely, both phase diagrams are topologically identical. However, it is clearly seen from Fig. 9b that for the AB two-scale multiblock copolymers (Fig. 2b) the region of the ordered phases stability lays at somewhat higher values of the effective Flory parameter $\tilde{\chi}$, describing the end blocks incompatibility, and the phase transition lines are shifted towards lower values of the middle block composition as compared to those for the ABC copolymers (Fig. 2a). This difference is due to the fact that the middle non-selective block is homogeneous in the case of ABC copolymers and heterogeneous in the case of two-scale multiblock AB copolymers. Accordingly, the middle block is *precisely* non-selective for the ABC copolymers but only *on average* non-selective for AB two-scale multiblock copolymers, and the fluctuations of the effective χ -parameter cause enhanced stability of the latter with respect to the ordering. Thus, the difference between the phase diagrams presented in Fig. 9a and Fig. 9b is a particular case of the more general fact^{45,46} that increase of a structural heterogeneity leads to enhancement of the system stability as to the order–disorder transition.

It is worth making three more remarks. First, the coordinates of the points in the plane $(f_C, \tilde{\chi})$ where the lines of the phase transitions LAM- G^A , G^A -D and D- S^A intersect the ODT line correspond precisely to the WST predictions.^{20,27,28} Second, beyond the ODT line vicinity the D phase stability has been verified thanks to the SCFT but the very idea of the diamond phase existence has been put forward based on the WST consideration^{19,20,27,28} (see also discussion in ref. 23). Third, the cylinder phase C^A with tetragonal packing is unstable within the WST²⁰ and, therefore, its existence, which is only due to the higher harmonics effect, could be detected only by using the SCFT.

Morphologies: visualization and connectivity

An idea of the spatial order parameter (composition) distribution under consideration in various triply periodic morphologies arising in the two-scale multiblock copolymers can be given by plotting the zero level surfaces calculated for the points 1–5 in Fig. 9b as well as estimating the corresponding topological permeabilities: *i*) the *alternating gyroid* is represented by two samples (see Fig. 10) corresponding to points 1 and 2 in Fig. 9b,

Fig. 9 Phase diagrams of the melts of symmetric block copolymers with a non-selective middle block. *a*) that for the ternary linear ABC block copolymer (reprinted with permission from ref. 25), left; *b*) that for the two-scale multiblock copolymer, right. The stability regions for the diamond and alternating gyroid, tetragonal planar and simple cubic phases are labeled as D, G^A , C^A and S^A , respectively. The dashed line in both phase diagrams corresponds to the transition to the disordered phase for the ternary ABC block copolymers. The bold line in the right phase diagram corresponds to the transition to the disordered phase for binary AB two-scale multiblock copolymer. The labeled points 1–4 correspond to the images shown in Figs. 10 and 11.

Fig. 10 Zero level surfaces for alternating gyroid morphologies existing at points 1 (a) and 2 (b).

the topological permeability being $q = 0.91$ and $q = 0.935$ at points 1 and 2, respectively (our estimate within the WST is $q = 0.9$); ii) the *diamond* is represented by two samples (see Fig. 11) corresponding to points 3 and 4 in Fig. 9b, the topological permeability being $q = 0.66$ and $q = 0.6$ at points 3 and 4, respectively; and iii) the zero level surface for *simple cubic* represented by point 5 in Fig. 9b looks very similar to that corresponding to the WST evaluation (see Fig. 3a and 4a) and we do not present it here. Nevertheless, the topological permeability at the real simple cubic morphology at point 5 is $q = 0.05$, which is much less than the WST $q_{SC}^{WST} = 0.33$.

It is seen from Fig. 10–11 that plotting zero level surfaces provides a good distinction between the topological (connectivity) properties of different lattices but it is certainly not the best tool to follow their evolution with increase of segregation.

However, this evolution can be traced making use of the topological permeability q . According to the data for q just presented, the connectivity is improving for the G^A phase and worsening for the D and S^A ones when the value of the corresponding χ -parameter (and, therefore, the degree of segregation) increases. To the best of our knowledge, introducing the topological permeability defined in our paper is the first attempt to provide a semi-quantitative estimation of the real morphologies' connectivity and its temperature evolution.

Fourier spectrum

Another way to quantitatively describe the ordering evolution within the phase diagram shown in Fig. 9b is to analyze the Fourier spectrum of the order parameter for all morphologies and its χ -dependence, which also allows us to find some special

Fig. 11 Zero level surfaces for diamond morphologies existing at points 3 (a) and 4 (b).

Fig. 12 The χ -dependence of the Fourier spectrum of the order parameter for the lamellar phase in molten two-scale multiblock copolymers with $f_B = 0.6316$. The curves corresponding to the amplitudes of the harmonics of the order $2n - 1$ are labeled by the integer n ; the dashed line clearly reveals that the 11th harmonic vanishes at $\tilde{\chi} \approx 87$.

extinction rules caused by the special architecture symmetry of the two-scale multiblock copolymers under consideration. For definiteness, we present the results of such an analysis for $m = 3.5$ ($f_B = 0.6316$).

For 1D LAM phase the order parameter Fourier series (3) takes the form

$$\Psi(z) = \sum_{k=1}^{\infty} A_k \cos(q_* k z + \varphi_k), \quad (18a)$$

where $q_* = 2\pi/L$ and L is the period. Due to the symmetry with respect to permutation of A and B monomers the order parameter (19) obeys an additional symmetry, which is expressed by equation

$$\Psi(z) = -\Psi(z + (L/2)), \quad (20)$$

where the origin $z = 0$ is assigned to the middle of a domain. This additional symmetry results in vanishing of all even harmonics:

$$\Psi(z) = \sum_{n=1}^{\infty} A_n \cos((2n - 1)q_* z + \varphi_n). \quad (18b)$$

Indeed, the amplitudes of the even harmonics appearing in (18a) that we calculated numerically are equal to zero (within the machine accuracy). The amplitudes of some of the odd harmonics as functions of $\tilde{\chi}$ are plotted in Fig. 12. It is worth noticing that i) the amplitudes $A_n(\tilde{\chi})$ of the higher harmonics (with $n > 1$) are rather small as compared to that of the dominant one (with $n = 1$), especially near the ODT, ii) some of the functions $A_n(\tilde{\chi})$ could have zeros within the interval of χ studied in this work.

The amplitudes of the first finite harmonics for the 2D tetragonal phase C^A and 3D simple cubic phase S^A are plotted in Fig. 13. In that case the order parameter Fourier series (3) takes the form

$$\Psi(z) = \sum_{\mathbf{n}} A_{\mathbf{n}} \cos(\mathbf{q} \mathbf{r} + \varphi_{\mathbf{n}}), \quad \mathbf{q} = q_* \mathbf{n}, \quad (21)$$

where $\mathbf{n} = (k, l, 0)$ and $\mathbf{n} = (k, l, m)$ for C^A and S^A , respectively, k, l, m are integers and summation in (21) runs over all corresponding

vectors $\mathbf{n}$. It should be stressed that vanishing of some harmonics allowed by the general symmetry of these lattices, *e.g.* (1,1) and (2,0) for C^A and (1,1,0) and (3,2,1) for S^A , resemble extinction of the even harmonics for the LAM phase. More precisely, the generalized extinction rule for the symmetric block copolymers is that all even $\S$ harmonics are equal identically to zero. It is worth noticing that harmonics of different order can belong to the same coordination sphere of the reciprocal lattice. In particular, it is seen in Fig. 13b that for the phase S^A the harmonics (2, 2, 1) of the 5th order (blue dashed) and (3, 0, 0) of the 3rd order (red dashed) as well as the harmonics (3, 2, 2) of the 7th order (green dotted) and (4, 1, 0) of the 5th order (blue dotted) belong to the same spheres of the radius 3 and $\sqrt{17}$, respectively.

Similarly, vanishing of some harmonics allowed by the general symmetry of the corresponding lattices is observed in the Fourier spectrum for the G^A and D phases presented in Fig. 14. In that case the order parameter Fourier series (4) takes the form

$$\Psi(\mathbf{z}) = \sum_{\mathbf{n}} A_{\mathbf{n}} \cos(\mathbf{q}\mathbf{r} + \varphi_{\mathbf{n}}), \quad \mathbf{q} = q^* (\mathbf{n}/c), \quad \mathbf{n} = n_1 \mathbf{q}_1 + n_2 \mathbf{q}_2 + n_3 \mathbf{q}_3, \quad (22)$$

where summation runs over all possible triples of integers (n_1, n_2, n_3). The generating vectors of the corresponding reciprocal lattice and normalization constant c appearing in eqn (21) read

$$\mathbf{q}_1 = (0, 1, 1), \quad \mathbf{q}_2 = (1, 0, 1), \quad \mathbf{q}_3 = (1, 1, 0), \quad c = |\mathbf{q}_1| = \sqrt{2} \quad (23a)$$

for the G^A phase and

$$\mathbf{q}_1 = (-1, 1, 1), \quad \mathbf{q}_2 = (1, -1, 1), \quad \mathbf{q}_3 = (1, 1, -1), \quad c = |\mathbf{q}_1| = \sqrt{3} \quad (23b)$$

Fig. 13 The χ -dependence of the Fourier spectrum of the order parameter for the phases C^A (a) and S^A (b) in molten two-scale multiblock copolymers with $f_B = 0.6316$. The curves are labeled by the corresponding integer vectors $\mathbf{n}$ defined after eqn (21) and colors are used to distinguish the 1st (black), 3rd (red), 5th (blue) and 7th (green) harmonics. The meaning of the dashed and dotted lines is described in text.

$\S$ We refer to the harmonics that are characterized by a wave vector $\mathbf{q}$, which can be represented as a sum of two wave vectors, which belong to the first coordination sphere of the corresponding reciprocal lattice, as the second harmonics. Generally, if the minimal number of the wave vectors, which belong to the first coordination sphere of the corresponding reciprocal lattice, necessary to sum to get $\mathbf{q}$ is equal to n , we refer to the harmonics characterized by the wave vector $\mathbf{q}$ as those of the order n .

Fig. 14 The χ -dependence of the Fourier spectrum of the order parameter for the phases G^A (a) and D (b) in molten two-scale multiblock copolymers with $f_B = 0.6316$. The curves are labeled by the corresponding integer vectors $\mathbf{n}$ defined in eqn (22) and (23) and colors are used to distinguish the 1st (black), 3rd (red) and 5th (blue) harmonics. The meaning of the dashed and dotted lines is described in text.

for the D phase. We found that, *e.g.*, the harmonics (2,0,0), (2,1,1), (4,2,0) for the G^A phase and (2,0,0), (2,2,0), (4,2,2) for the D phase are equal to zero within the computer accuracy. Again, it is seen in Fig. 14 that, *e.g.*, the harmonics (3, 3, 0) of the 3rd order (red dashed) and (4, 1, 1) of the 5th order (blue dashed) for the phase G^A as well as the harmonics (3, 3, 3) of the 3rd order (red dashed) and (5, 1, 1) of the 5th order (blue dashed) for the D phase belong to the same coordination spheres, respectively.

The generalized extinction rule for the symmetric block copolymers can be easily understood within the framework of the weak segregation Hamiltonian (14). Indeed, as mentioned above, due to the very symmetry with respect to the exchange $A \leftrightarrow B$ of the copolymer architecture under study, the cubic (in powers of Ψ) term in the Hamiltonian (14) vanishes identically, which makes the generation of the second harmonics impossible. The fact that all even harmonics vanish rather than the second ones only means that this property stays conserved under iterative solution of the non-linear SCFT equations.

To summarize, the data on the Fourier spectrum of the order parameter in the studied phases confirm the WST symmetry predictions and we witnessed that within the phase diagram region we studied all ordered phases are weakly or moderately segregated.

Lattice spacing

The last assertion is also supported by the dependence of the lattice period L on $\tilde{\chi}$ we calculated *via* the SCFT and present in Fig. 15. Within the interval of the χ -values covered in this study, we see a monotonous increase of L with increase of χ for each phase, which is typical for most of the studied AB block copolymers. However, the phase transitions G^A –D and D– C^A are accompanied by some jump-like decreases of L (in the former case the jump is practically unseen). One should also keep in mind that the two-scale architecture of block copolymers $A_{mN/2}(B_{N/2}A_{N/2})_nB_{mN/2}$ could result in a new sort of morphology transition (the *structure-in-structure* transition), which may be accompanied by a non-monotonous dependence $L(\chi)$ as shown³⁰ for 1D *lamellar-in-lamellar* transition. So, one can expect that the further increase of χ would be also accompanied by a non-monotonous behavior of $L(\chi)$ due to the occurrence of *structure-in-structure* morphologies possessing the 2D symmetry C^A or 3D symmetry SC or G^A . We aim to study this effect in more detail elsewhere.

Fig. 15 The χ -dependence of the period L measured in units of the whole chain gyration radius $R = a\sqrt{N(n+m)}/6$ for the diamond, gyroid, C^A and lamellar phases (solid line) for $m = 3.3$, $n = 6$ ($f_B = 0.645$). Vertical dotted lines indicate the values of the reduced χ -parameter corresponding to the G^A -D and D- C^A phase transitions. In the range where a phase is stable (metastable) the corresponding plots are drawn as the solid bold (dashed) lines.

5. Conclusion

The present paper continues theoretical studies^{20,23,27–29} of the order–disorder and order–order transitions in block copolymers, whose peculiarity is the replacement of the conventional^{17,39,40} lamellar phase by various (depending on block copolymer architecture) cubic phases. Here we calculated, *via* the SCFT numerical procedure, the phase diagram of the two-scale AB multiblock copolymers and compared it with that of the linear ternary ABC block copolymers. For both copolymers the phase diagrams are topologically equivalent, their most striking feature being the presence of two morphologies, alternating gyroid and diamond, which are characterized by the presence of 3D clusters providing, unlike the conventional anisotropic lamellar and cylindrical phases, the isotropic percolation along the cluster channels. Therewith, the OPLS visualization, $\tilde{\chi}$ -dependence of the lattice spacing and Fourier spectrum data witness that within the $\tilde{\chi}$ -interval studied ($\tilde{\chi} < 90$) no *structure-in-structure* formation occurs. Similar phase diagrams are expected in all cases when the middle part of a block copolymer is effectively non-selective with respect to the tails (*e.g.* if the middle block is a random AB copolymer) even though they could somewhat differ quantitatively. To estimate the expected permeability of such morphologies a new quantity (topological permeability) is introduced and calculated. The results presented open a new route to design ordered block copolymer morphologies with high permeability both in bulk and thin films. Due to a difference in the symmetry properties (the G^A phase does not possess any mirror planes whereas the D phase does) it is the D phase which is expected to provide good connectivity (and, thus, transport) properties in thin films. We will address this issue in more detail elsewhere.

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