Defect Patterns from Controlled Heterogeneous Nucleations by Polygonal Confinements

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ABSTRACT: Defects are often observed in crystalline structures. To regulate the formation or annihilation of defects presents an interesting question. In this work, we propose a method to fabricate defect patterns composed of regularly distributed steady “programmed defects”, which is proceeded via the heterogeneous nucleation of a hexagonal pattern from a homogeneous state. The nucleation process occurring in a model system of AB-diblock/C-homopolymer blends under polygonal confinement is modeled by the time-dependent Ginzburg–Landau theory and is simulated by the cell dynamics simulations. Specifically, we demonstrate the validity of this method by means of three polygonal confinements including square, pentagon, and octagon, which have mismatched angles with the hexagonal lattice. Each corner or side of the polygons induces a nucleation event separately. Two nucleated domain grains by two neighboring corners or sides exhibit incommensurate orientations, and thus their merging leads to a radial line of clustered defects in the form of five–seven pairs. As a result, these radial lines constitute a radial pattern of defects, and their number is equal to the side number of the polygon. The distance of five–seven defect pairs is dictated by the incommensurate angle between two neighboring grains, which is similar to that of defects in hard crystals. This method can be extended to fabricate diverse defect patterns by programming the nucleation agents beyond simple polygonal confinements.

INTRODUCTION

Crystals have become one of the most useful types of materials for humans because of their ordered structures, which exhibit a lot of remarkable properties in contrast to amorphous materials. Accordingly, crystalline structures have attracted intensive research interest from the whole scientific society. Nowadays, the concept of crystals has been broadened from conventional hard materials to soft condensed materials, that is, soft crystals. Soft crystals are usually formed by the self-assembly of various subunits, including colloids,1–4 amphiphilic macromolecules,5–10 and DNA or peptide-tethered nanoparticles,11–13 which are termed nanocrystals or mesocrystals. The crystal constant dictated by the size of the subunit ranges from nanometer to micrometer and therefore is much larger than that of hard crystals. A large crystal constant facilitates the visualization of soft crystals in experiments, thus making them sensitively responsive to thermal fluctuations as well as external fields. On the one hand, the responsiveness to thermal fluctuations increases the probability of formation of crystallographic defects. On the other hand, the responsiveness to external fields offers opportunities for one to control the fabrication of soft crystals.

In hard crystals, defects have been intensively studied. It has been demonstrated that defects are not always harmful, although they destroy the perfection of crystals by breaking the translational or rotational order. In many crystalline materials, defects are purposely introduced to play unique roles.14–16 Similarly, defects in soft crystals have also attracted a lot of interest.17,18 In particular, a lot of efforts have been dedicated to studying the stability of defects occurred in the ordered nanostructures self-assembled by block copolymers (BCPs),19–26 which are referred to as mesocrystals.10 There are two main aims for this study. One aim is to obtain perfect mesocrystals by annihilating defects or avoiding the occurrence of defects via external guiding patterns, that is, directed self-assembly (DSA) of BCPs.27–31 In the contrary, the other one is to make irregular structures by stabilizing defects via DSA.32–35 Both defect-free patterns and defective structures are potentially applicable in the semiconductor industry.17,36

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Usually, defects are metastable or unstable because an energy penalty is associated with the formation of defects, which is referred to as the excess free energy of defect (denoted as $E_d$). At the same time, an energy barrier $E_b$ needs to be overcome to remove a metastable defect. Accordingly, defects with high energy barrier can survive for a long time or even become permanently steady as their lifetime $\tau_{lif}$ at temperature $T$ is proportional to $\exp(E_b/k_B T)$, where $k_B$ is the Boltzmann constant. To obtain various steady defects represents an interesting but also challenging problem. Furthermore, if the distribution of steady defects could be programmed into desired defect patterns, it may provide a promising perspective for applications.\(^{15-17,32,37,38}\)

It has been known that defects are usually caused on the boundary of two grains with mismatched lattice orientations. The annihilation of these clustered defects is through a coarsening process in which small grains are absorbed by larger grains.\(^{17,32,37,38}\) The annihilation of these clustered defects is through a coarse-graining process in which small grains are absorbed by larger ones. Accordingly, each domain grain is determined by its neighbors because its growth at each direction terminates when its shape of each domain grain are determined by its neighbors. In a word, desired defect patterns can be obtained by tailoring the size, positions, and orientations of associated crystalline domain grains.

An efficient way to produce single crystalline grains with controlled positions and orientations is via a heterogeneous nucleation process,\(^{14-48}\) in which nucleation events are induced by imposed nucleation agents and then nucleated domains grow into defect-free domain grains. The position and orientation are solely dictated by those of the nucleation agents that are controllable in practice. Moreover, the size and shape of each domain grain are determined by its neighbors because its growth at each direction terminates when its advancing front meets with those of its neighbors. In a word, desired defect patterns can be obtained by tailoring the position distribution and orientations of the nucleation agents. Thus, it may be more appropriate to refer to this type of defects as "programmed defects".

In the literature, spontaneous nucleations have been observed in different phenomenological model systems, which are based on the Ginzburg–Landau theory.\(^{36,49,50}\) Specifically, one of the phenomenological models was originally developed for the diblock copolymer/homopolymer (AB/C) blending system by Ohta and Ito.\(^{51}\) In this system, the nucleation process is described by the Cahn–Hilliard dynamic equations (model B) based on the time-dependent Ginzburg–Landau (TDGL) theory, which can be efficiently solved using the cell dynamics simulation (CDS). Then, heterogeneous nucleations were realized in a few systems where nucleation agents were acted as potential wells and corner/sidewall of geometrical confinements.\(^{44,46,48}\) In fact, the qualitative conclusions derived from the model should hold for other crystalline systems because all nucleation phenomena share the classical nucleation theory.\(^{52}\)

In this work, we focus on the fabrication of defect patterns via the heterogeneous nucleations occurred in the two-dimensional AB/C system simulated by CDS based on the TDGL theory. In the two-dimensional space, the stable hexagonal crystalline phase nucleates from the metastable disordered state. Geometrical confinement has become not only an efficient way of modifying the self-assemblies of BCPs for more novel ordered structures but also useful nucleation agents.\(^{53-64}\) Here, the nucleation agents are simply chosen as various regular polygonal confinements, including triangular, rectangular, polygonal, hexagonal, and octagonal. The triangular and hexagonal geometries have commensurate angles with the hexagonal lattice, whereas the others do not. Accordingly, each corner or sidewall of the rectangular, pentagonal, and polygonal confinements with appropriate surface interactions is able to induce one nucleation domain independently. The nucleated domain grains by different corners or sidewalls have different orientations, leading to the occurrence of clustered defects on their boundaries. As a result, these regularly distributed clusters of defects assemble into interesting defect patterns.

### THEORY AND METHODS

We consider a model system originally developed for the binary blend composed of AB-diblock copolymer and C-homopolymer (AB/C), which is laterally confined in a regular polygon well. This AB/C blend is specified by the volume fraction of C-homopolymer, $\phi_C$, and the block ratio of the A-block in the AB-diblock copolymer, $f$. Two independent order parameters are needed to characterize the phase separation of the three-component system, which are chosen as the two density differences, $\phi(\mathbf{r}) = \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})$ and $\eta(\mathbf{r}) = \phi_B(\mathbf{r}) + \phi_C(\mathbf{r}) - \Psi_0$, where $\phi_A(\mathbf{r}) (K = A, B)$ denotes the volume fraction of the K-component at position $\mathbf{r}$ and $\Psi_0$ is a constant. On the basis of the Ohta–Kawasaki model,\(^{65}\) the free-energy functional of the system is expressed as

$$F[\phi, \eta] = F_1[\phi, \eta] + F_2[\phi, \eta] + \int d\mathbf{r} H_{\text{int}}(\mathbf{r}) \phi(\mathbf{r})$$

where the short-range interaction term $F_1$ originating from the well-know Ginzburg–Landau free energy is written as

$$F_1[\phi, \eta] = \int d\mathbf{r} \left\{ \frac{D_1}{2} [\nabla \phi(\mathbf{r})]^2 + \frac{D_2}{2} [\nabla \eta(\mathbf{r})]^2 + f_\phi(\phi) + f_\eta(\eta) \right\} + f_{\text{int}}[\phi, \eta]$$

Here, $D_1$ and $D_2$ are two positive constants. The last three terms on the right-hand side of the above expression are contributed by the cross interactions between the three components. For the reason of convenience, the derivatives of $f_\phi$ and $f_\eta$ are given as $d f_\phi/d\phi = -\lambda_0 \tanh\phi$ and $d f_\eta/d\eta = -\lambda_3 \eta$ where $\lambda_0 > 1$ and $\lambda_3 > 1$. $f_{\text{int}}$ consists of a number of intercrossing terms of $\phi$ and $\eta$ and is given by

$$f_{\text{int}} = b_1 \eta \phi - b_2 \eta \phi^2/2 - b_3 \eta \phi^3 - b_4 \phi^4 + b_5 \eta^4/2$$

where $b_i$ ($i = 1, 2, 3, 4$) are constants.

In eq 1, the long-range term $F_2$ stems from the connectivity between the A- and B-blocks and is written as

$$F_2[\phi, \eta] = \int d\mathbf{r} d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') \left\{ \frac{\alpha}{2} \delta\phi(\mathbf{r}) \delta\phi(\mathbf{r}') + \beta \delta\phi(\mathbf{r}) \delta\eta(\mathbf{r}') + \gamma \delta\eta(\mathbf{r}) \delta\eta(\mathbf{r}') \right\}$$

where $\delta\phi(\mathbf{r}) = \phi(\mathbf{r}) - \bar{\phi}$ and $\delta\eta(\mathbf{r}) = \eta(\mathbf{r}) - \bar{\eta}$ with $\bar{\phi}$ and $\bar{\eta}$ being the spatial average of the two order parameters, respectively. The coefficients $\alpha$, $\beta$, and $\gamma$ satisfy the relation of $\beta = \gamma \sigma_0$. In the above expression, the Green function $G(\mathbf{r}, \mathbf{r}')$ with a Coulomb interaction form characterizes the long-range feature of the chain connectivity of the diblock copolymer.

In the last term on the right-hand side of eq 1, $H_{\text{int}}(\mathbf{r})$ quantifies the preferential interactions of the sidewalls, which is given by

$$H_{\text{int}}(\mathbf{r}) = \frac{1}{2} \lambda_3 \left[ \text{tanh} \left( \sigma - d(\mathbf{r})/\epsilon \right) + 1 \right]$$

where the shortest distance of the position $\mathbf{r}$ to any sidewall of the polygon $d(\mathbf{r}) < 2\sigma$. The field strength, interaction distance, and potential steepness are denoted by $\lambda_3$, $2\sigma$, and $\epsilon$, respectively. Note
that we assume that all sidewalls in each polygon have equal surface potential.

With the free-energy functional in eq 1, the phase separation dynamics of the AB/C blend is described by the conserved Cahn–Hilliard dynamic equations:

$$\frac{\partial \phi}{\partial t} = M_1 \nabla^2 \delta \bar{F}[\phi, \eta] + \xi_\phi(r, t)$$

(5)

$$\frac{\partial \eta}{\partial t} = M_2 \nabla^2 \delta \bar{F}[\phi, \eta] + \xi_\eta(r, t)$$

(6)

where $M_1$ and $M_2$ are two mobility coefficients and $\xi_\phi$ and $\xi_\eta$ are the noise terms, which satisfy the fluctuation dissipation theorem.

Note that this model system contains many parameters, all of which have explicit physical meanings when the model is referred to the specific AB/C blending system. As we mainly make use of the capability of nucleations of crystalline phases from a uniform state to produce controlled crystalline grains, we do not give a detailed discussion on these parameters. However, more detailed information can be found elsewhere. Here, we simply use the values of these parameters similar to those in our previous work, that is, $f = 0.4$, $D_0 = 0.5$, $D_1 = 1$, $M_1 = M_2 = 1$, $A_b = 1.26$, $A_f = 1.10$, $b_1 = -0.05$, $b_2 = 0.05$, $b_3 = 0.01$, $b_4 = 0.10$, $W_1 = 0.20$, $\sigma = 0.15$, and $r_0 = 0.5$, where $L_0$ is the crystal constant of the crystalline phase. Additionally, $\phi_c$ is fixed as $\phi_c = 0.025$, ensuring that the spontaneous nucleation as a rare event would not disrupt the growth of heterogeneous nucleations. Similar to our previous work, we reduce the system to be two-dimensional, where the crystalline phase is hexagonal. The standard discretization scheme of CDS is employed to solve the dynamic equations. Our source codes are available on the website of GitHub.

### RESULTS AND DISCUSSION

It has been known that there are two types of heterogeneous nucleations induced by the polygonal confinement, that is, side-induced and corner-induced, which are controlled by the strength of the attractive surface interaction $\Lambda$. It has been demonstrated that the corner can induce nucleations with a higher rate than the side. In other words, the corner-induced nucleation events occur before the side-induced ones when increasing $\Lambda$. For either of corner-induced or side-induced nucleation in the $n_g$-gonal confinement, the orientations of two nucleated domain grains induced by two neighboring corners or sides differ in a given angle, $\Delta \theta = 360/n_g$ degrees. If $\Delta \theta$ is multiples of $60^\circ$, the neighboring grains have coherent orientations and thus they may merge into a single crystalline grain. Otherwise, defects are unavoidably caused on their merging boundary. Obviously, the triangular and hexagonal confinements ($\Delta \theta = 120^\circ$ and $60^\circ$) are commensurate in the angle for the hexagonal pattern, whereas the other polygonal confinements, such as square, pentagon, and octagon, are not. In the following, we will discuss the angle-matched and angle-mismatched cases separately.

**Angle-Matched Polygonal Confinements for Ordered Patterns.** As we mainly focus on the fabrication of defect pattern, here, we only briefly discuss the heterogeneous nucleations occurred in the angle-matched triangular and hexagonal confinements. More systematic results can be found in our previous work. The main aim of this part of work is to provide a direct contrast to the heterogeneous nucleations induced by angle-mismatched polygonal confinements. In Figure 1, typical morphologies generated via the corner- and side-induced nucleation processes in an equilateral triangular confinement with a side length of $L = 50.5L_0$ are shown. The corner-induced nucleation occurs with a weak field strength of $\Lambda_0 = 0.002$, whereas the side-induced one occurs with a stronger field strength $\Lambda_0 = 0.005$ because the corner can induce nucleation with a higher nucleation rate than the side according to the classical nucleation theory. Moreover, the classical nucleation theory indicates that the corner with a smaller angle leads to a higher nucleation rate.

The corner- and side-induced nucleation events are clearly evidenced by an isolated domain grain at each corner in the morphology snapshot in Figure 1(a1) at $t = 5.5 \times 10^5$ and multiple domains at each side/corner in the morphology snapshot in Figure 1(b1) at $t = 1.5 \times 10^5$, respectively. Note that the highly different times in Figure 1(a1),(b1) originate from the different incubation times of the corner- and side-induced nucleations. When these domain grains grow up to fill the entire triangle at the moment $t_{fill} = 7.2 \times 10^5$, the three corner-induced domain grains merge into a single crystalline hexagonal pattern in Figure 1(a2) because of their consistent orientations. In contrast, the merging of the side-induced domain grains leads to a few isolated five-seven-defect pairs (or dislocations). The main cause is that multiple nucleations are induced at random locations along each side. The increased number of nucleations without coherent locations increases the occurrence probability of defects. The similar results are also observed in the hexagonal confinement (Figure 2). As the contrast of the nucleation rates at the corner and at the side for a specific phase separation system confined in a given geometry is solely controlled by the field strength $\Lambda_0$, the ordering degree of the final pattern should depend on $\Lambda_0$. In Figure 3a, the defect concentration $\langle J_{\Pi \Psi} \rangle$, defined as $n_{\Pi \Psi}/n_{DMN}$ with $n_{\Pi \Psi}$ being the number of five-seven-defects and $n_{DMN}$ being the number of domains, is calculated as a function of $\Lambda_0$ for a given triangle with $L = 50.5L_0$. In this triangular confinement, the defect-free hexagonal pattern consists of $n_{DMN} = 1098$ domains. This result indicates that the defect-free pattern is achieved as long as the corner-induced nucleation domains fill the entire triangle for $\Lambda_0 \leq 0.0025$, which implies
nucleation process. To examine the size effect, even for the ideal corner-induced defect-free pattern when the hexagonal size is incommensurate as the in nucleation rate increases. When \( \Lambda_0 \) becomes larger than 0.005, the nucleation rate at the side becomes high enough to make the incubation time very short. In other words, the heterogeneous nucleations at the sides and at the corners occur almost simultaneously, and as a result, the merging of their grown domain grains causes a certain amount of defects because of their incoherent positions, that is, \( \langle f_{DP} \rangle = 0.8 \pm 0.2\% \).

Our previous work reveals that there are size commensurability windows, even for the fabrication of defect-free hexagonal patterns via the heterogeneous nucleations in the hexagonal confinement.46 This means that it is hard to obtain defect-free pattern when the hexagonal size is incommensurate with the domain spacing, even for the ideal corner-induced nucleation process. To examine the size effect of the triangular system, we calculate \( \langle f_{DP} \rangle \) as a function of the side length of the triangle \( L \) for three typical values of \( \Lambda_0 = 0.002, 0.005, \) and 0.007 (Figure 3b). Interestingly, the defect concentrations do not exhibit observable dependence on \( L \). In particular, \( \langle f_{DP} \rangle \) is consistently zero for \( \Lambda_0 = 0.002 \), indicating that there is no size incommensurability for large triangular systems. This observation is in big contrast to the limited size commensurability windows in the hexagonal system. The higher tolerance of the triangular system to the size incommensurability than the hexagonal system may originate from the strong confining effect and directing ability.

### Angle-Mismatched Polygonal Confinements for Defect Patterns

After examining the heterogeneous nucleations induced by the angle-matched polygonal confinements, which lead to the patterns with no defect or a small number of isolated five–seven defect dislocations, we turn to examine those in the angle-mismatched polygons. Thus, the heterogeneous nucleation by the angle-matched polygonal confinements is not able to form defect patterns composed of regularly distributed defects, so we turn to examine the heterogeneous nucleations under the angle-mismatched polygonal confinements.

One of such simplest regular polygons is square. Our previous work has revealed that the heterogeneous nucleation process in a rectangular/square confinement can lead to the formation of defect-free hexagonal pattern when the two pairs of parallel sides of the rectangle or square have unequal field strengths.48 Accordingly, here, we focus on the situation that all sides of the square confinement have equal field strength, exhibiting equal inducing nucleation rates.

In Figure 4, three different types of heterogeneous nucleation processes are observed in the square confinements with different field strengths, resulting in the formation of distinct morphologies composed of single, double, or multiple crystalline domain grains. For weak \( \Lambda_0 = 0.002 \), both nearly defect-free (Figure 4a) and defective (Figure 4b–d) morphologies are observed. Interestingly, three defective morphologies exhibit three different regular defect distributions: 90° corner (Figure 4b), cross (Figure 4c), and straight line (Figure 4d). Obviously, these defect-clustered boundaries in each morphology delimit domain grains with different orientations indicated by the white-line hexagons.

Our previous work suggested that these nucleations should be corner-induced.46 Usually, for the corner-induced nucleation, the hexagonal array of domains prefers to align the plane (e.g., (10)) with the highest density of domains (designated as HDD plane) along each side to minimize the surface energy. However, the corner angle of the square confinement is

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**Figure 2.** Morphology snapshots under the confinement of a regular hexagonal confinement with the side length of \( L = 30.5L_0 \) similar to those in Figure 1. (a1) \( t = 3.8 \times 10^3 \) and (a2) \( t = 1.5 \times 10^4 \) for the corner-induced nucleation with \( \Lambda_0 = 0.002 \) in the top row; whereas (b1) \( t = 1.5 \times 10^3 \) and (b2) \( t = 6.4 \times 10^3 \) for the side-induced nucleation with \( \Lambda_0 = 0.005 \) in the bottom row.

**Figure 3.** (a) Average defect concentration of the hexagonal pattern \( \langle f_{DP} \rangle \) as a function of \( \Lambda_0 \) formed by the heterogeneous nucleation process in the triangular confinement with a fixed side length \( L = 30.5L_0 \) (b) \( \langle f_{DP} \rangle \) as a function of \( L \) for various \( \Lambda_0 = 0.002, 0.005, \) and 0.007. Note that each point and its standard deviations are obtained by averaging the data on eight independent simulation samples.
incommensurate with the hexagonal lattice. If both sides of a corner induce the HDD plane, each corner must induce two domain grains with different orientations. As a consequence, defects are caused on the boundary of the two grains, which are energy cost. When the gain of the surface energy from the alignment of the two HDD planes is not enough to compensate the excess free energy of defects, the induction of two domain grains at each corner is unfavorable. Therefore, only single crystalline grain is formed at each corner of the square confinement with weak $\Lambda_0 = 0.002$ in Figure 4a–d, which aligns its HDD plane along either of the two sides stochastically with equal probability. The defect-free pattern is formed when the four domain grains at the four corners have consistent orientation, and otherwise various regular defect patterns are obtained. The theoretical probabilities of obtaining the defect patterns (b2), (c2) and (d2) are counted as 50, 12.5, and 25%, respectively.

When $\Lambda_0$ is increased to 0.0025, the surface energy becomes comparable to the excess free energy of defects, and thus double crystalline grains are observed at the top right corner of Figure 4(e1). This special morphology gives rise to a special distribution of defects, forming a 45° corner. For high $\Lambda_0 = 0.007$, the surface energy becomes dominant over the excess free energy of defects, and accordingly, every corner induces double crystalline domain grains, whose merging results in the formation of the defect pattern of a tilted cross (Figure 4(f2)). In contrast to the defect patterns in Figure 4b–e, which are formed with certain probabilities, the distribution of defects into the tilted cross is deterministic when $\Lambda_0 > 0.003$. It is interesting to notice that double crystalline domain grains delimited by a grain boundary have been observed within a 90° edge in a pioneering experiment by Segalman and co-workers.19

The second confining geometry with a mismatched angle considered here is the regular octagon with a vertex angle of 135°. Similar to the case in the pentagonal confinement, radial defect patterns are obtained from both the corner-induced and side-induced nucleation processes because of the inconsistent orientations of these nucleated domain grains (Figure 6). However, there is an obvious difference between the two cases in the pentagonal and octagonal confinements, which lies in the defect patterns formed by the corner-induced nucleation processes. In the former case, each radial line points to the center of the side, whereas that in Figure 5(b2) points to the vertex.

The third confining geometry with a mismatched angle considered here is the regular octagon with a vertex angle of 135°. Similar to the case in the pentagonal confinement, radial defect patterns are obtained from both the corner-induced and side-induced nucleation processes because of the inconsistent orientations of these nucleated domain grains (Figure 6). However, there is an obvious difference between the two cases in the pentagonal and octagonal confinements, which lies in the defect patterns formed by the corner-induced nucleation processes. In the former case, each radial line points to the center of the side, whereas that points to the vertex in the latter case. This difference is due to the fact that single and double crystalline domains are induced by each corner in the pentagonal and octagonal confinements, respectively. Compared with the pentagonal confinement with an angle deviation of 12° from 120° of the hexagonal lattice, the octagonal confinement has a larger angle deviation of 15°. A larger angle deviation may cause a higher energy penalty associated with the
deformation of the single crystalline domain lattice. As a result, the single crystalline grain is split into double crystalline grains at each corner. Thus, defects are enriched on the radial boundary of the twin grains.

In hard materials, it has been established that the distance between the five and seven defect pairs (or dislocations) enriched on the boundary between two neighboring grains with a mismatched angle $\theta$ is determined by $d_{DL} = a_0/[2 \sin(\theta/2)]$, where $a_0$ is the lattice constant and $a_0 = L_0$ in the current system. This relation may hold for this soft-domain mesocrystal, although the soft deformable domain is very different from atoms. To test this hypothesis, we first devise a test model system which consists of only two domain grains with a controllable mismatched angle. In practice, we set up two pairs of double-well attractive potentials to act as the nuclei, which are tilted $\pm \theta/2$ relative to the horizontal axis (Figure 7a). The two nuclei induce two nucleation domain grains synchronically.$^{44}$ As a consequence, the mismatched angle between two domain grains is $\theta$. When the nucleated domain grains grow up to fill the entire sample, defects are produced and arranged into a straight line. Thus, the distance of dislocations can be calculated. The data of $d_{DL}$ obtained in the test model system are in good agreement with the theoretical formula (Figure 7a). Furthermore, the data of $d_{DL}$ of defects formed in these polygonal confinements satisfy the theoretical relation well (Figure 7b). This observation confirms that the theoretical relation between the distance of defect dislocations and the mismatched angle between two neighboring grains is rather robust for either hard or soft crystalline systems.$^{39,40}$

\[ d_{DL} = \frac{a_0}{2 \sin(\theta/2)} \]

\[ d_{DL} = \frac{L_0}{2 \sin(\theta/2)} \]

It is necessary to note that the deformation of soft domains produces strain around them that usually propagates into a number of domain spacings. This implies that these defect pairs would interact with each other within a rather long distance and thus their distance is changed by the long-range interaction to deviate slightly from the theoretical prediction, especially when these defect pairs approach each other at the central region of the polygons.

**CONCLUSIONS**

In summary, we propose a simple method of fabricating defect patterns in crystalline structures, which are composed of regularly distributed defects, via a heterogeneous nucleation process. The validity of this method is demonstrated by means of the nucleations of the hexagonal ordered phase from the disordered state in an AB-copolymer/C-homopolymer model system, where the nucleations are induced by various regular polygonal confinements. The phase separation kinetics is simulated by the CDIs based on the TDGL theory. Our simulation results demonstrate that the defect-free hexagonal patterns could be obtained in the polygons whose vertex angle is matched with the hexagonal lattice including the regular triangle and hexagon, whereas a variety of defect patterns are generated in the polygons with mismatched vertex angles such as square, regular pentagon, and octagon.

Figure 6. Morphology snapshots formed in the octagonal confinement with a side length $L = 30.5L_0$ for $L_0 = 0.009$ (b1,b2). (a1) $t = 3.8 \times 10^5$ and (a2) $t = 8.8 \times 10^5$; (b1) $t = 1.5 \times 10^5$ and (b2) $t = 6.6 \times 10^5$.

Figure 7. (a) Comparison of distance of defect dislocations between the theory $[d_{DL} = a_0/(2 \sin(\theta/2))]$ (solid line) and a purposely devised test model system (symbols) that consists of two domain grains generated by a heterogeneous nucleation process, induced by two nuclei acted as by two pairs of double-well potentials, of which each pair is tilted $\theta/2$ relative to the horizontal axis. (b) Comparison of $d_{DL}$ between the theory and the simulations on the systems under the square, pentagonal, and octagonal confinements.

![Graphical representation](image-url)
In general, the boundary of the polygons with mismatched vertex angles is able to trigger two kinds of heterogeneous nucleations, corner- and side-induced nucleations, which often result in different defect patterns. For the side-induced nucleations by a strong surface field, where each side induces a nucleation domain grain independently, the regular radial defect patterns are formed with the number of radial lines equal to the number of sides and each radial line pointing to the vertex. In contrast, the defect patterns from the corner-induced nucleations by a weak surface field are more changeable because the number and orientation of the nucleated domain grains at each corner depend on the vertex angle. For the square confinement, a single crystalline grain is formed at each corner with the HDD plane (e.g., the (10) plane) randomly aligned along one side of the corner but normal to the other side. This implies that the different combinations of orientations of the domain grains at the four corners would lead to different defect patterns including 90° corner, cross, and a straight line parallel to one side. Interestingly, in the pentagonal confinement, the domain lattice is deformed to fit into the mismatched corner, thus leading to a single crystalline domain grain with one HDD plane at every side of the corner. As a result, the radial defect pattern with each radial line normal to the side is formed as these domain grains at the five corners meeting with each other. In contrast, in the octagonal confinement, the large angle mismatch leads to the formation of double crystalline domain grains, resulting in the radial defect pattern with each radial line pointing to the vertex, which is similar to that formed by the side-induced nucleations.

In conclusion, this work demonstrates an efficient method of tailoring the defect distribution via the controlled heterogeneous nucleations by the polygonal confinement, leading to the formation of interesting defect patterns. On the one hand, this concept can be expanded further to program the locations of nucleation agents for more desired defect patterns that may have potential applications in many fields such as photonic crystals and nanotechnology. On the other hand, the conclusions from this model system should hold for other crystalline systems.

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**Notes**

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