# Cell Crystals: Kelvin's Polyhedra in Block Copolymer Melts

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Using Monte Carlo simulations we find that a monodisperse symmetric *ABCD* star-block copolymer melt undergoes a microphase separation, in which the three space is divided into cellular domains. The domain shape is a cubooctahedron known as the Wigner-Seitz cell of the body-centered cubic lattice. To be precise, the shape is a Lord Kelvin's minimal tetrakaidecahedron proposed in 1887 for the space-filling problem of equal-sized foam bubbles. [S0031-9007(98)08139-3]

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Block copolymers comprising chemically distinct polymers linked together are intriguing, because microphase separations of block copolymer melts provide superb periodic morphologies: lamellar, bicontinuous, cylindrical, and spherical phases [1,2]. A common feature in these morphologies, which is not usually mentioned, is that at least one component occupying large blocks of copolymers is unbounded in space, such as a matrix in a spherical or a cylindrical phase. In this paper, using Monte Carlo simulations, we show that a cellular and periodic morphology appears in microphase separations of symmetric "*ABCD*" star-block copolymer melts. In the structure, all components form spatially bounded cellular domains. Because periodic elements are cells instead of atoms, we refer to the structure as a "cell crystal" and the phase as a "cell (crystalline) phase," whose lattice constant is nanoscale of the order of $10-10^2$ nm, the domain sizes of microphase separations.

Cell division is a fundamental geometric problem in various phenomena: bubble forms, biological cells, metal crystallites [3,4]. In the history of the investigations, the Kelvin's minimal tetrakaidecahedron [5] has occupied a central position, because it had been considered as the best solution of the following problem: What arrangement of cells of equal volume minimizes the total surface area of the cell walls? After more than a hundred years, this age-old solution was defeated by Weaire and Phelan [6]: They showed that the Kelvin's tetrakaidecahedron was not minimal. We intend to revive the Kelvin's polyhedra in a different system having the same physical driving force, namely, minimizing surface area.

To explain why star tetrablock copolymers are required for the division of the three space, we consider a role of blocks of copolymers in view of cell division. As shown in Fig. 1(a), the one-dimensional space is divided into segments by symmetric *AB* block copolymers due to immisibility of different blocks of block copolymers; the natural realization is the lamellar phase, where each domain extends to infinity in two dimensions. In Fig. 1(b), using symmetric *ABC* star block copolymers having an additional *C* component, the two-dimensional space is separated into hexagons embedded in the honeycomb pattern. Obviously, the honeycomb structure is a minimal cell division of the two space. This structure has been observed in a simulation [7]. Each domain still extends to infinity in one dimension.

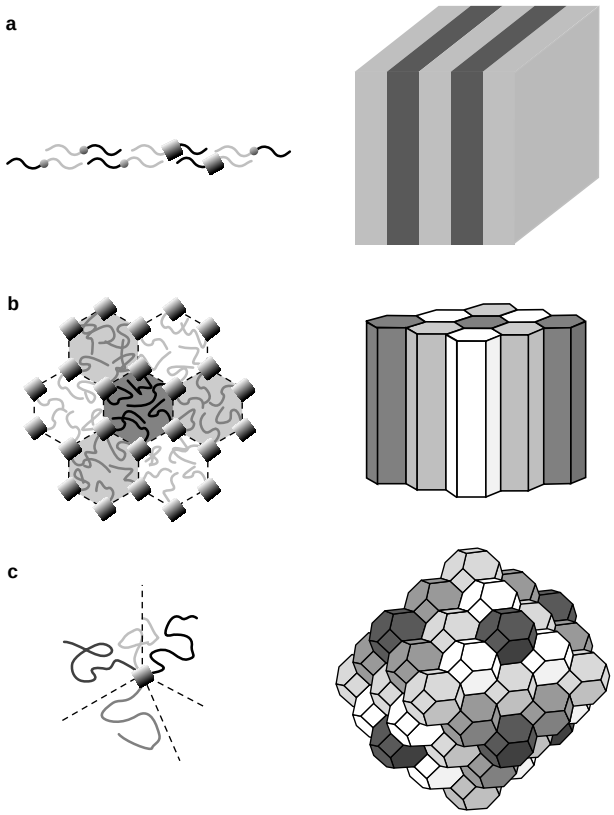


FIG. 1. Division of $d$-dimensional space ($d = 1, 2, 3$) by symmetric $(d + 1)$-arm star block copolymers. (a) *AB* diblock copolymers: The 1-space is divided into alternating segments (left), forming a lamellar phase in the 3-space (right), where each component extends two dimensionally. (b) *ABC* star triblock copolymers: The 2-space is divided into hexagons composing a honeycomb structure (left), where each component is unbounded in the 3-space (right). (c) *ABCD* star tetrablock copolymers (left): The 3-space is divided into polyhedra called cubooctahedra, which are well known as the Wigner-Seitz cells of the body-centered cubic lattice. Each component is compactly bounded in the 3-space (right).

  

Notice that at least four polyhedra should meet at a point for polyhedral space filling; this is why cell division has not been observed under three components. Now a key question is whether the three-dimensional space can be divided by symmetric *ABCD* star block copolymers or not. We have found that the answer is affirmative as illustrated in Fig. 1(c): a space-filling structure made up of cubooctahedra (truncated octahedra), known as the Wigner-Seitz (Voronoi) cell (or the Diriclet region) of the body-centered cubic lattice [8].

Our method is a lattice polymer Monte Carlo simulation method called the "diagonal bond method," which serves morphology study of microphase separations in particular [7]. Although details of the method are given in Ref. [7], we briefly mention several merits of the method. (1) Lattice models including our model can deal with many polymer systems. (2) We employ face and body diagonals of cubes as bonds; thereby the lattice model acquires a large number of configurations and elementary moves. (3) While the lattice model maintains excluded volume and pair interactions between monomers, it allows bond crossings and phantom moves, which result in a considerable increase in the mobility of polymers. (4) We can carry out simulations of star polymers. These features enable us to form microphase separated morphologies from high temperature randomized configurations.

A model copolymer consists of two agents denoted $Y$ and arms as shown in Fig. 2. Here the number of polymers in a system is determined such that the occupation ratio of monomers in the lattice points is 0.75. We assume that 25% vacancies act as nonselective good solvents. To represent energetics that drive the system to microphase separation, unit interaction energies are imposed only between nearest neighbor and diagonal pairs of different components: We consider the Hamiltonian as $H = \sum \epsilon_{\alpha\beta}$, where $\epsilon_{\alpha\beta} = 1$ when $\alpha \neq \beta$, and $\alpha$ and $\beta$ stand for $A$, $B$, $C$, $D$, or $Y$.

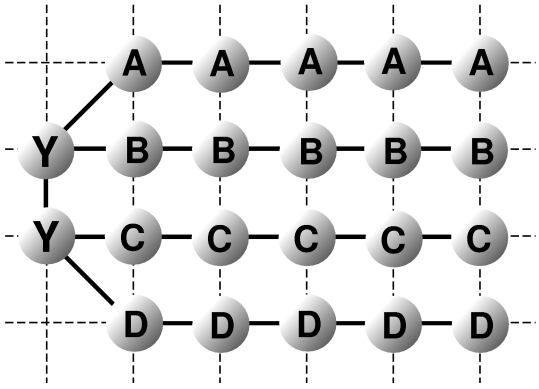


FIG. 2. A model symmetric *ABCD* star block copolymer. $Y$ denotes an agent from which three bonds branch. The block lengths of four components are the same. Although the model polymer does not have permutation symmetry of four components, we have prepared (almost) an equal number of densities of three different combinations in a simulation cube.

We have examined box sizes $L^3$ with $L = 16$–$46$ and have made ordered structures at $\beta\ (= 1/k_BT) = 0.08$–$0.1$ for the case of star copolymers having nine monomers in each arm ($N = N_A = N_B = N_C = N_D = 9$). Figure 3(a) is a simulation result for a size $L^3 = 46^3$ at $\beta = 0.3$, well below the order-disorder transition temperature. Regions of $A$, $B$, $C$, and $D$ monomer densities

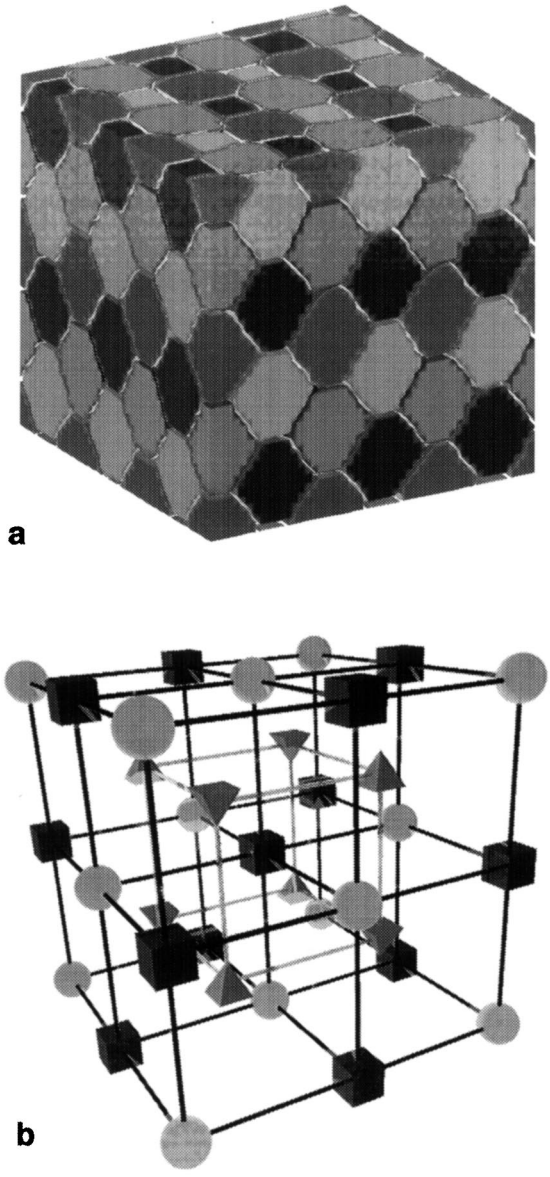


FIG. 3. (a) Cell crystal: Surface view of a simulation box ($L^3$ with $L = 46$). Numbers of monomers in each arm are $N = N_A = N_B = N_C = N_D = 9$, and the number of copolymers in the cube is $N_P = 1921$; the occupation ratio of monomers in lattice points is 0.75. The box size has fallen into $3/\sqrt{2} \times 3/\sqrt{2} \times 2$ times a unit cell of the system. (b) Unit cell of the cell crystal: Polyhedral domains are represented by symbols. The Bravais lattice is the face-centered cubic lattice. $A$ (sphere) and $B$ (cube) components form a simple cubic lattice, and $C$ (upward pyramid) and $D$ (downward pyramid) components form a simple cubic lattice on the $AB$ cube body centers; both constitute a body-centered cubic lattice.

averaged over 50 000 Monte Carlo steps are displayed. It is obvious that the structure is crystalline and by careful observations we find that the space-filling structure is nothing but one illustrated in Fig. 1(c). In order to match the periodic boundary conditions, structures for box sizes with $L \geq 40$ are tilted and distorted; however, as far as we have done, all simulations have exhibited the same structure.

Figure 3(b) represents a unit cell of the system, where symbols correspond to cell centers. The Bravais lattice of the system is the face-centered cubic lattice, and the unit structure is described by $A$ $(0,0,0)$; $B$ $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; $C$ $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$; $D$ $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$. The space group is $F\bar{4}3m$. The permutation symmetry of four components is broken in this structure, since two components constitute one simple cubic lattice and the other two make up the other simple cubic lattice. Therefore, there are three topologically different ordered states: $(A,B)$-$(C,D)$, $(A,C)$-$(B,D)$, and $(A,D)$-$(B,C)$. There will be accordingly three kinds of domain walls. Although we suppose that these walls may hinder the nucleation and the growth of an ordered structure, in each simulation of our sizes, a single state has covered the entire system with long simulation processes ($<10^6$–$10^7$ Monte Carlo steps).

The polyhedron is not simply plane faced at low temperatures, because it tends to minimize its surface area to reduce interfacial energies between different components. We point out that the shape is the Kelvin's minimal tetrakaidecahedron. For minimal surface cell division, four boundary lines of interfaces should meet at a point $P$ such that the angle $\theta$ between two lines is $109° 47'$ ($\cos\theta = -1/3$); in other words, tangent vectors of four lines emanating from $P$ point to four vertices of a regular tetrahedron. To attain this restriction, squares on the cubooctahedron are plane faced but surrounded by curved arcs, becoming a little more like circles. Then hexagons are not plane faced but wavy with keeping zero-mean curvature, namely, negative Gaussian curvature. In this way, the Kelvin's polyhedron is constructed and it becomes a little more like a sphere.

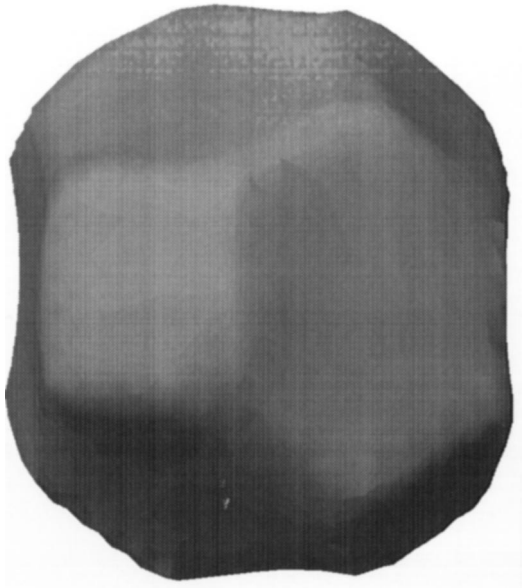

FIG. 4. Close view of one domain in a simulation. Number of monomers in each arm is 40 ($N = 40$). The number of copolymers is $N_P = 296$ in a box $L^3$ with $L = 40$, whose size corresponds to one unit cell of the system. The polyhedron relates to the Kelvin's minimal tetrakaidecahedron. Notice that hexagons are not exactly plane faced.

Figure 4 displays an interface of one cell obtained in a simulation: The number of monomers in each arm is $N = 40$ and the number of copolymers is $N_P = 296$ in a cube $L^3$ with $L = 40$. The ordered structure was produced at $\beta = 0.02$. To see a low temperature structure, we averaged monomer densities over 50 000 Monte Carlo steps at a very low temperature ($\beta = 0.3$). One can see in Fig. 4 that hexagons are not plane faced as expected by Kelvin. We have checked that the mean curvatures ($H$) of the interface rendered in Fig. 4 are almost zero (Fig. 5) except on edges and vertices, and we have estimated that 73% of the total surface has negative Gaussian curvature ($G$). Since four cells associated with four components join at vertices of cells, agents concentrate near the points. Thus in Fig. 4 surfaces at vertices are not sharp, but rounded.

There is a crucial difference between bubble and star tetrablock copolymer systems: In the case of star tetrablock copolymers, faces composing polyhedra should be even-numbered polygons, because coloring polyhedra by four colors around an odd-numbered polygon is impossible. Very recently Weaire and Phelan have given a better solution to the above mentioned Kelvin's problem by using the $\beta$-tungsten (or A15) structure [6]. It is clear that their structure should not appear in our system, since they have employed polyhedra having pentagonal faces. In

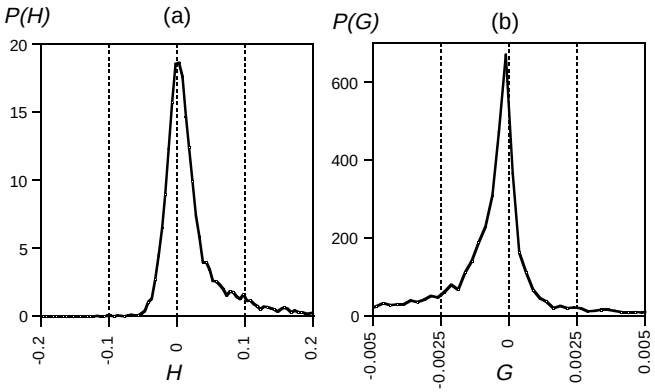


FIG. 5. Distributions (a) $P(H)$ and (b) $P(G)$ of the local mean ($2H = 1/R_1 + 1/R_2$) and Gaussian curvatures [$G = 1/(R_1R_2)$] over the cell surface rendered in Fig. 4, where $R_1$ and $R_2$ are the principal radii of curvature. The main part of $P(H)$ has a peak at zero, implying the minimal surface character; accordingly, the large part of $P(G)$ is negative, while the positive tail of $H$ (or $G$) stems from edges and vertices (or vertices) of the cell.

the same way, Frank-Kasper phases or tetrahedrally close-packed structures [9] are not candidates for our system. Only the Kelvin's polyhedron satisfies this requirement.

Recently a number of experiments has been done for star triblock copolymers [10], while there are few studies on star tetrablock copolymers [11]. Beyond the imagination of Kelvin, the experimental realization of a cell crystal is awaited. Furthermore, asymmetry of star arms may produce different crystalline structures, and nonequilibrium cell phases including noncrystalline mosaic structures are also expected. We anticipate that the application of star tetrablock copolymers will give a new dimension to design and fabricate materials.

[1] F. S. Bates, Science **251**, 898 (1991).
[2] F. S. Bates and F. S. Fredrickson, Annu. Rev. Phys. Chem. **41**, 525 (1990).
[3] P. S. Stevens, *Patterns in Nature* (Little, Brown Company, Boston, 1979).
[4] R. Williams, *The Geometrical Foundation of Natural Structure* (Dover, New York, 1979).
[5] W. Thomson (Lord Kelvin), Philos. Mag. **24**, 503 (1887).
[6] D. Weaire and R. Phelan, Philos. Mag. Lett. **69**, 107 (1994); see also *The Kelvin Problem, Foam Structures of Minimal Surface Area*, edited by D. Weaire (Taylor & Francis, London, 1996).
[7] T. Dotera and A. Hatano, J. Chem. Phys. **105**, 8413 (1996).
[8] B. K. Vainshtein, *Modern Crystallography I* (Springer-Verlag, Berlin, 1981).
[9] N. River, Philos. Mag. Lett. **69**, 297 (1994).
[10] S. Okamoto, H. Hasegawa, T. Hashimoto, T. Fujimoto, H. Zhang, T. Kazama, and A. Takano, Polymer **38**, 5275 (1997); A. Takano, M. Ueno, T. Araki, T. Kazama, and Y. Isono, Polym. Prepr. Jpn. **46**, 2630 (1997); T. Araki, A. Takano, T. Kazama, and Y. Isono, Polym. Prepr. Jpn. **47**, 675 (1998); S. Sioula, N. Hadjichristidis, and E. L. Thomas, Macromolecules **31**, 5272 (1998); S. Sioula, N. Hadjichristidis, and E. L. Thomas, Macromolecules **31**, 8429 (1998). Unfortunately, none of these studies has clearly shown the honeycomb structure.
[11] H. Iatrou and N. Hadjichristidis, Macromolecules **26**, 2479 (1993).