Polymeric Quasicrystals

— Dodecagonal quasicrystal in ABC star block copolymers —

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ABC星型ブロック共重合体の格子高分子モデルのモンテカルロ・シミュレーションによって，12回対称準結晶(近似結晶)の形成に成功した。以下の特徴が観察された。(1) フーリエ変換（構造関数）はほぼ12回対称性を示す。(2) Stampfli変換による自己相似性が観察される。(3) ランダムに形態変化や合体分離を繰り返しながらもグローバルな12回対称性は保存する。(4) (3) はタイリングの入れ替えに対応する準結晶特有のフェイゾン・ダイナミクスとみなせる。(5) よく知られた12回対称性正三角形-正方形タイリングよりもランダウ理論から導かれる密度波の構造と一致する。最近，合金のFrank-Kasper相（σ相）に関連した80nmの辺の長さを持つ正三角形，正方形からなる3^2434アルキメデスタイリング構造が実験的に発見されているが，この構造は常に準結晶相に隣接して現れる構造である。このことと合わせ，高分子準結晶の発見が期待される。

1 Simulation Results

We have found the formation of an large approximant of a dodecagonal quasicrystal (DDQC) in a lattice Monte Carlo simulation of ABC star block copolymer melts[1,2]. Results are summarized as follows: (1) The MC averaged structure function shown in Fig.1(a) is almost 12-fold. (2) We find local 12-fold wheel patterns in Fig1(a). The centers of the wheels form a self-similar lattice: The edge length is about 300nm, when the experimental value is assumed[3]. (3) Cells are dynamically rearranged and deformed, and consequently the wheels change their positions, which dynamics does not break the global symmetry and sharp diffraction peaks. (4) This collective dynamics can be viewed as a rearrangement of the square-triangle tiling, known as phason dynamics, which is the crucial degree of freedom that quasicrystals have. (5) Contrary to the usual square-triangle tiling, there is no six-fold node. Rather, the simulation resembles the density wave pattern (Fig.1(b)) of C component obtained from a Landau theory.

2 Discussion

The polymeric quasicrystal is a fundamentally new phase of soft matter. So far, no quasicrystalline phases have been found in polymeric systems. However, a recent striking advance in

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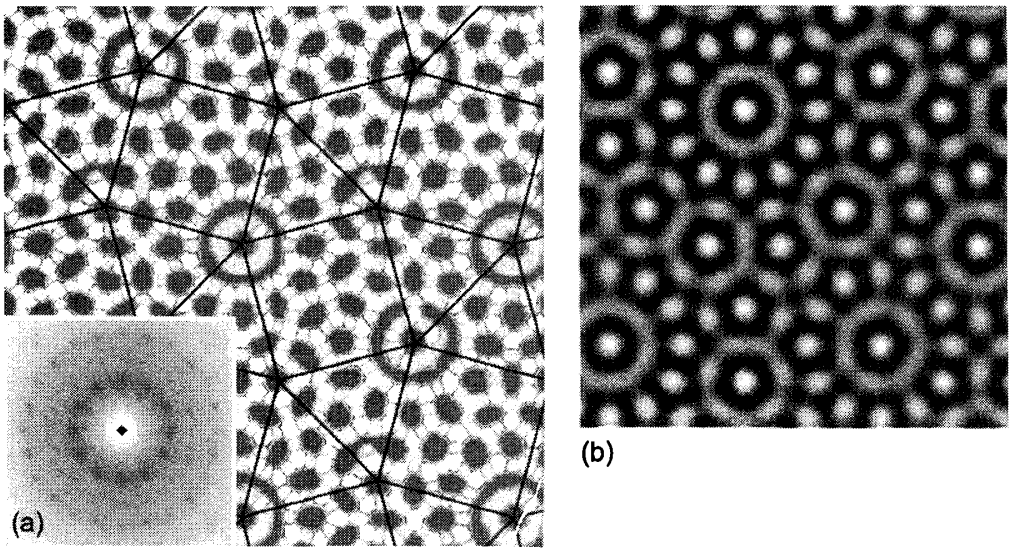

Figure 1: (a) Simulation result for A9B7C16 star block copolymers in a Box with $128^2 \times 10$: A (white), B (light) and C (dark). A two-periodic unit cell made up of four replicas is rendered. Twelve-fold wheel patterns construct a Stampfli scaled (3^2.4.3.4) lattice (solid line). The pictures represents the volume rendering of averaged densities over 10^3 MCS at a quenched temperature. The inset is the thermal averaged structure function for the C component, where almost 12-fold peaks are observed. (b) The density wave description for the C component obtained from a Landau theory.

the experiment of ABC starblock terpolymers[3], which shows the Archimedean tiling (3^2.4.3.4) consisting of triangles and squares, related to the σ phase in the Frank-Kasper family, [2] and therefore the result indicates the possibility of the DDQC.

We finally list the size growth for tiling edges of the σ phases: metallic alloy (∼0.5nm), chalcogenide (∼2nm), dendron (∼10nm) and star block copolymer (∼80nm). Hence we are going to ask: Can quasicrystals be universal over different length scales? If so, do they form with the same origin? The present result is not only fundamental progress in soft matter physics, but also may give a deep insight into hard condensed matter physics.

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References

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[2]It is known that near quasicrystalline phases, there exist complex crystalline Frank-Kasper phases.