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Long-Lived Metastable bcc Phase during Ordering of Micelles

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We report a metastable bcc phase that intervenes between a disordered micellar suspension and an fcc crystal in a block copolymer solution. Upon heating, the metastable bcc phase nucleates first, and then transforms over the course of hours to the stable fcc phase. At still higher temperatures, the fcc phase transforms to an equilibrium bcc phase. These results constitute an interesting experimental manifestation of Ostwald's step rule, and also support recent theory and simulation results whereby bcc nucleates more readily from a melt of spheres.

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Crystallization of spherical particles is a universal and fascinating phenomenon. Representative examples varying widely in chemical nature and size include simple atoms, surfactant and block copolymer micelles, and colloids. While the equilibrium phase behavior is often well understood, important kinetic features such as nucleation or growth and the associated nucleation pathways are not fully understood. One canonical example is nucleation in hard-sphere and Lennard-Jones fluids, where face-centered cubic (fcc) is the stable phase. Many theories and simulations have been performed on the nucleation and growth of supercooled fluids [1–7]. The pioneering theory was formulated by Ostwald in 1897. His "step rule" suggests that the solid phase which nucleates first is not necessarily the thermodynamically stable phase, but rather is the one with its free energy closest to that of the fluid phase [1]. More recently, Alexander and McTague proposed that, at least for small supercooling, the body-centered cubic (bcc) phase should nucleate first in all simple fluids that exhibit weakly first-order melting transitions [2]. There have been several attempts to explore the Alexander-McTague scenario by simulation [3–7]. However, the results are somewhat contradictory; for the Lennard-Jones system, in which the fcc phase is stable, some simulation studies found only the formation of fcc nuclei [6,7], while others observed a metastable bcc phase [3–5]. This controversy has been attributed to the very large degrees of supercooling imposed on the crystal formation, due to the limited time scale of the simulation [4]. In this case, it is possible that the free energy barriers for the nucleation of all crystal phases become small. The formation of crystal nucleation at modest undercooling was studied by ten Wolde *et al.* [4], who found that the precritical nuclei are bcc, which then transform to the critical fcc nuclei. This was confirmed by Shen and Oxtoby using density functional theory [5]; they found that a bcc character appears between the stable fcc phase and the liquid.

Experimentally, a metastable bcc phase has been observed in rapidly quenched metals. For example, Cech found that a metastable bcc phase was formed first in an Fe-Ni alloy, although the fcc phase was stable over the entire temperature range [8]. Similarly, a metastable bcc phase was found in other metal alloys, such as Fe-Ti-Si [9], Fe-Co [10], and Ni-V [11]. In contrast, as far as we are aware such an observation has not been reported in soft materials, e.g., block copolymers and colloids. However, it should be possible in block copolymers, given that such systems have shown a propensity to develop relatively long-lived transient or metastable structures [12,13]. In this Letter, we demonstrate that, in a suitably chosen solution, block copolymer spherical micelles also follow Ostwald's step rule and form a metastable bcc phase on the way to a stable fcc phase. Interestingly, the same solution exhibits a second bcc phase at higher temperatures, but in this case the bcc lattice is stable.

A symmetric poly(styrene-*b*-isoprene) (SI) diblock copolymer was synthesized by anionic polymerization [14,15]. A combination of size-exclusion chromatography and NMR spectroscopy established the block molecular weights to be 15 200 and 15 400 g/mol, respectively, with an overall polydispersity index of 1.02. The isoprene-selective solvent squalane (C30) was used as received (Aldrich). A single solution with polymer volume fraction $\phi = 0.20$ was prepared gravimetrically, and examined by rheology and small angle x-ray scattering (SAXS) as a function of temperature. Remarkably, a sequence of five distinct phases was observed upon heating: a disordered solution of spherical micelles → bcc → fcc → bcc → disordered solution of chains. The two order-order transitions (OOTs) and two order-disorder transitions (ODTs) were suggested by the dynamic moduli, G' and G'', as a function of temperature (Fig. 1) using a Rheometric Scientific ARES rheometer (1 rad/s, 1% strain, 1 °C/min). The negligible moduli below 50 °C and above 170 °C signify disordered solutions, and the sharp changes in the moduli at these temperatures reveal first-order ODTs, as is well established [16]. The "reentrant" nature of this ordered phase window is unusual but has been noted before [14,15]. Within the ordered

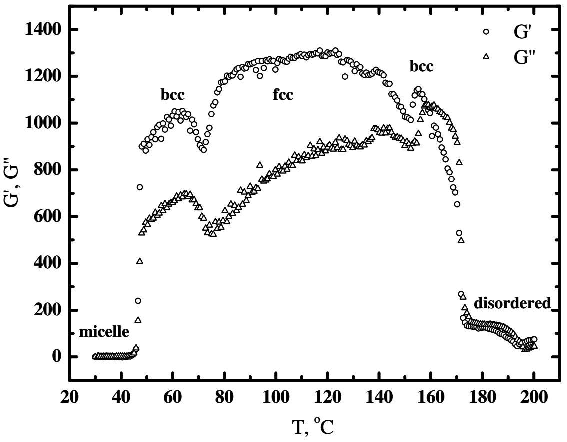


FIG. 1. Isochronal temperature dependence of the dynamic moduli, G' and G'', at frequency 1 rad/s, strain 1%, and 1 °C/min.

state, there are two local minima evident in both moduli, one near 75 °C corresponding to a bcc → fcc OOT, and one near 150 °C due to the reverse fcc → bcc OOT. For OOTs between the fcc and bcc phases, one might expect rather little change in the dynamic moduli, but the observed minima can plausibly be attributed to a transient, partially liquidlike state as the lattices rearrange. Interestingly, there is an overall arc to the ordered state moduli, especially evident in G', with a broad maximum near 120 °C. This feature can be directly correlated to the density of micelles, as revealed through the principal peak position, q^*, discussed below. In other words the increase/decrease in modulus is due to a decreasing/increasing lattice constant.

Figure 2 shows representative SAXS patterns as intensity I versus wave vector q obtained on the University of Minnesota 2 m beam line (as described elsewhere [14,15]). At 25 °C, the absence of any higher order peaks confirms that the solution is a disordered suspension of micelles. The SAXS pattern is dominated by the principal structure factor peak at q^*, with clear evidence of the form factor of spherical micelles in the first minimum and maximum near 0.045 and 0.055 Å^{-1}, respectively. A hard-sphere form factor is shown as the dashed line, for comparison purposes. Upon heating to 60 °C, the micelles pack onto a bcc lattice as shown by the peaks at q/q^* ratios of $1{:}\sqrt{2}{:}\sqrt{3}{:}\sqrt{7}$; allowed reflections at $\sqrt{4}$, $\sqrt{5}$, and $\sqrt{6}$ are suppressed by the form factor minimum. Based on a small angle neutron scattering study of the temperature dependence of similar micelles in dilute solution, we proposed that this reentrant ODT is induced by a small increase in the micellar dimension, due to slight swelling of the core by the solvent with increasing temperature [17]. The bcc phase then transforms to the fcc phase upon heating, as identified at 100 °C by the peaks at relative positions at $\sqrt{3}{:}\sqrt{4}{:}\sqrt{8}{:}\sqrt{11}{:}\sqrt{19}{:}\sqrt{20}$. (The first pair and the last pair of peaks are not fully resolved due to the instrumental resolution.) The fcc phase persists up to high temperature, until it transforms to the bcc phase again at 160 °C. The solution was then finally disordered by 180 °C. The inset of Fig. 2 shows $q^*(T)$ for the same solution.

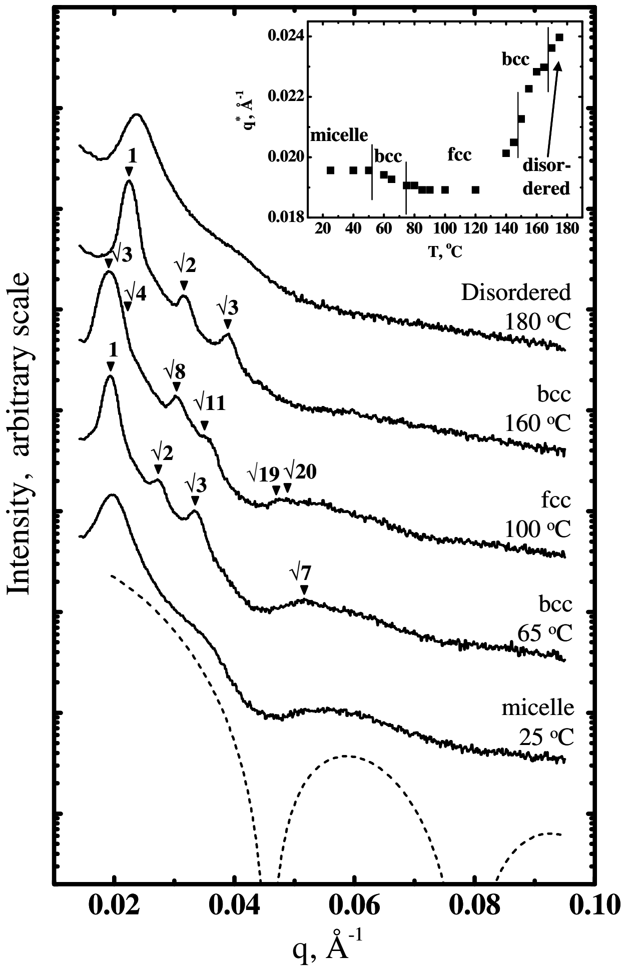


FIG. 2. Representative SAXS profiles as a function of temperature. The phase sequence is disordered micelles → bcc → fcc → bcc → disordered with increasing temperature. The inset shows the temperature dependence of the principal peak position. The dashed line corresponds to a hard-sphere form factor with a radius of 98 Å.

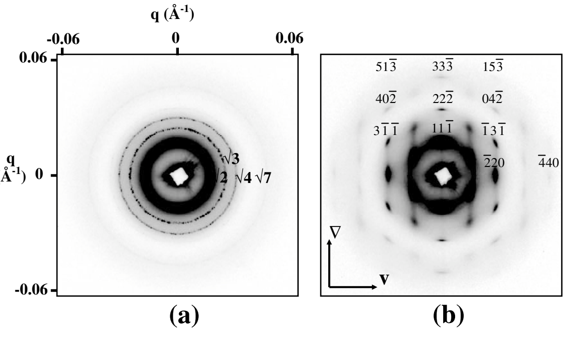
Of the two OOTs, the higher temperature fcc → bcc transition is identical to that which we have characterized fully in related solutions. It is thermally reversible and epitaxial [17–20], and the transformation pathway is identical to that established in several atomic systems [18,19]. This transition was shown to be driven by a decrease in the aggregation number (and an increase in the number density) of micelles, as the solvent selectivity decreases with increasing temperature, leading to a softer intermicellar potential [17,20]. In fact, the aggregation number at the transition is in good agreement with calculations for highly branched star polymers [21]. From the inset of Fig. 2 it can be seen that the transition occurs when the micelle-micelle nearest-neighbor distance is decreasing significantly, as the reduced aggregation number allows closer packing (of a larger number) of micelles. Most importantly, this high temperature bcc lattice is established to be an equilibrium phase.

The lower temperature bcc phase is the focus of this Letter. Although there is no *a priori* reason why it could not be an equilibrium phase, it would be very surprising. First, the solvent selectivity decreases with increasing temperature, and thus the aggregation number also decreases; this favors the fcc to bcc transition, not the reverse. Second, although a thermotropic bcc to fcc transition was reported by Hamley and co-workers, it was attributed to a contraction of the corona, as in their system the solvent quality decreases with increasing temperature [22]. This is not the case here, as the polystyrene corona blocks are always under good solvent conditions. Third, this transition is observed in the region where the micellar dimensions are nearly temperature independent [17]. Although the reentrant ODT was previously ascribed to the slight increase in the micellar size by the solvent swelling, it is unlikely that such a subtle change also affects the intermicellar potential significantly. Accordingly, we now consider the hypothesis that the low temperature bcc phase is actually metastable, with fcc the equilibrium state. Three further experiments were performed:

(i) Gentle oscillatory shear was applied to the bcc phase. The effects of shear on fcc and bcc micellar phases have been well documented [23], and such shearing should yield the corresponding pattern for the bcc phase, if it is stable.

(ii) The solution was annealed at a temperature within the bcc phase to see if there is any morphological change.

(iii) The solution was quenched from the fcc phase to the bcc phase, and then annealed to examine the reversibility between the fcc and bcc phases.



(a) (b)

FIG. 3. SAXS patterns at 65 °C along the vorticity (**e**) direction (a) before shearing (bcc) and (b) after shearing (fcc/hcp). Indexing in (b) corresponds to fcc along [112] [i.e., velocity (**v**)-shear gradient (**∇**) plane, where $\mathbf{v} = [11\bar{1}]$ and $\boldsymbol{\nabla} = [1\bar{1}0]$]. Indexing for hcp and further details can be found in Refs. [19,25].

Oscillatory shear was applied on the solution at 65 °C, as shown in Fig. 3. For this experiment, a modified cone-and-plate shear cell [24] was installed on Station 5-ID-D at the DND-CAT at the Advanced Photon Source at Argonne National Laboratory. Figure 3(a) displays the SAXS pattern immediately before the inception of shear. The isotropic rings at the relative q/q^* positions $1{:}\sqrt{2}{:}\sqrt{3}{:}\sqrt{4}{:}\sqrt{7}$ clearly indicate the bcc phase (again the $\sqrt{5}\ q^*$ and $\sqrt{6}\ q^*$ reflections are not observed due to extinction by the form factor minimum). Immediately upon shearing the solution (1 rad/s and 100% strain for 10 min), a SAXS pattern with well-developed "spots" was obtained [Fig. 3(b)]. This particular scattering pattern is characteristic of closed-packed spheres, i.e., a mixture of fcc and hcp, as documented previously [18,19]. (Note that the scattering patterns of fcc/hcp in the vorticity direction are identical, and thus all the spots are a superposition of reflections from fcc and hcp.) The more detailed indexing of this pattern can be found elsewhere [19,25]. The closed-packed phases remain unchanged after 1 h of shearing. These results are strong evidence that the bcc phase is metastable; the small applied perturbation is apparently sufficient to "knock" the system over the barrier.

The annealing experiments confirm this view. Figure 4 shows the SAXS patterns at 65 °C after 5 min, and then after 2, 3, 4, and 8 h annealing. The clear $\sqrt{2}\ q^*$ and $\sqrt{3}\ q^*$ reflections indicate the bcc phase at 5 min, and then the $\sqrt{3}\ q^*$ reflection becomes smeared out after 2 h. After 3 h of annealing, the $\sqrt{2}\ q^*$ reflection also began to diminish, and a hint of the $\sqrt{8}/\sqrt{3}\ q^*$ fcc reflection was observed as shown by the arrow. The $\sqrt{2}\ q^*$ reflection diminished further after 4 h, and disappeared after 8 h (see dashed line). Concurrently, the $\sqrt{8}/\sqrt{3}\ q^*$ reflection became clearer after 4 h, and then intensified further along with the $\sqrt{11}/\sqrt{3}\ q^*$ reflection after 8 h, implying that the complete transformation to the fcc phase is achieved. It should be also noted that there is essentially no change in the principal peak position, q^*, over the entire annealing time (see inset of Fig. 4). This supports the metastability of the bcc phase in the sense that this transformation occurs without changes in micellar characteristics, but only in their spatial arrangement. Finally, the solution was quenched to 65 °C from a well-developed fcc phase at 100 °C. Even after a day of annealing, the scattering patterns of the fcc phase remained unchanged (data not shown). These three experiments collectively confirm that the low temperature bcc phase is actually metastable with respect to fcc.

This block copolymer solution provides a clear experimental demonstration of the Alexander-McTague conjecture, i.e., that a metastable bcc phase can form spontaneously near the melting line upon gradual temperature change from the disordered phase, and then transforms to the stable fcc phase. This particular illustration of

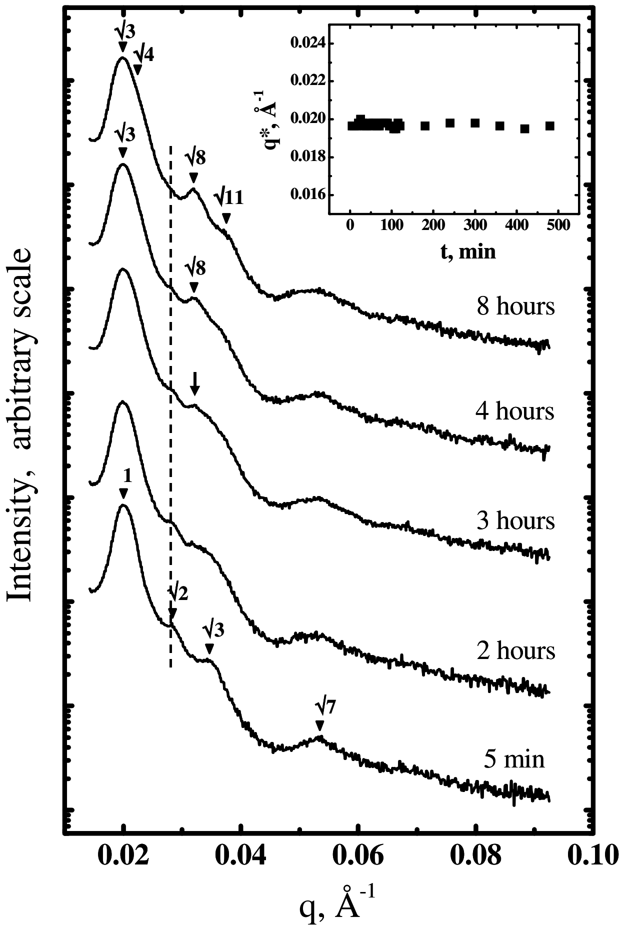


FIG. 4. SAXS profiles as a function of annealing time at 65 °C. The inset shows the time dependence of the principal peak position.

Ostwald's step rule in the soft materials is the first of which we are aware. The striking similarity to experimental observations in atomic systems, and to simulations of "ideal" hard-sphere systems, confirms the universality of the phenomenon. It is interesting to speculate as to why the metastable bcc phase is so long-lived in this system. It is presumably related to the sluggish kinetics of rearrangement of the micelles, given that their coronas are significantly overlapped in the less efficiently space-filling bcc phase.

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