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Kinetics versus thermodynamics dichotomy and growth mechanisms in linear self-assembly of mixed nanoblocks

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ABSTRACT

Self-assembly is a low energy synthesis process, prominent in biological systems, in which smaller building blocks spontaneously associate to form highly organized structures of great complexity. Thus, it is one of the most promising strategies to engineer hierarchical functional nanostructures. Of special interest are one-dimensional arrays of nanobuilding blocks (e.g., nanoparticles, peptides, colloids, etc.), such as nanowires, nanotubes or polymer-like structures, due to their potential applications ranging from nanosensing, optoelectronics, or molecular selective transport to mechanical reinforcement in structural composites. However, despite considerable advances on the synthesis side in the past few years, there is lack of understanding of the physics underlying the self-assembly kinetics and the mixing of diverse building blocks in low-dimensional structures. Short-term kinetic mechanisms of growth (in the order of nanoseconds to milliseconds) are difficult to reach with computationally intensive molecular simulations and yet occur too rapidly to be resolved with experiments. The growth mechanisms and kinetics of systems such as peptide nanotubes remain unexplored. Regarding supramolecular organization, the effect of kinetic traps on the formation of arrested phases is not yet fully understood, particularly in systems where self-assembly is driven by enthalpic interactions and nonequilibrium configurations are prevalent. Here, we present recent results from classical and replica exchange molecular dynamics simulations that establish the mechanisms underpinning the growth kinetics of a binary mix of nanorings that form striped nanotubes via self-assembly type. We show that a step-growth coalescence model captures adequately the growth process of the nanotubes, which suggests that high-aspect ratio nanostructures can grow by obeying the universal laws of self-similar coarsening, contrary to existing belief that growth occurs exclusively through nucleation and elongation (e.g., amyloid fibrils). Notably, we found that striped patterns do not depend on specific growth mechanisms, but are governed by tempering conditions that control the likelihood of depropagation and fragmentation.