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Pathway Complexity in Supramolecular Polymerization of Peptide Amphiphiles

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In supramolecular systems, pathway complexity enables access to metastable and kinetically trapped states, offering control over material properties. Adjusting experimental conditions allows supramolecular polymerization to yield tailored structures and diverse morphologies from identical precursors. This study examines pathway complexity in the supramolecular polymerization of peptidic, water-soluble Zn(II) porphyrin building blocks using experimental and computational approaches. Two peptide designs, glycine (G) and phenylalanine (F), were studied: a rigid GF_3 sequence and a flexible G_2F_3 sequence. Both include a PEG domain for water solubility and thermoresponsive behavior. The rigid GF_3 sequence undergoes rapid, spontaneous polymerization over a wide temperature range, while G_2F_3 polymerizes only above 40 °C due to an activation barrier. To investigate polymerization mechanisms, a coarse-grained model with planar bead-based monomers and parameters like interaction strength, bead size, and linker flexibility was developed. Simulations showed that stronger interactions enhance polymerization, while flexibility hinders it due to steric effects. While the model predicts a power-law relationship between polymerization half-times and monomer concentrations, experimental results suggest more complex mechanisms. A free energy model revealed a linear relationship between binding free energy and bond number, with stiffer monomers forming more stable polymers. Hybrid Molecular Dynamics Monte Carlo simulations aim to map the free energy across polymer sizes and generate a phase diagram to further explore structure formation across system parameters.