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Peptide Length Determines Equilibrium Secondary Structure in Protein-Analogous Micelles MATTHEW TIRRELL, University of Chicago, RACHEL MARULLO, Cooper Vision, MARK KASTANTIN, University of Colorado — This work seeks improved bottom-up design of bioinspired materials built from peptide-amphiphiles, which are a class of bioconjugates whereby a biofunctional peptide is covalently attached to a hydrophobic molety that drives self-assembly in aqueous solution. Specifically, this work highlights the importance of peptide length (i.e. molecular weight) in determining the equilibrium secondary structure of the peptide as well as the self-assembled (i.e. micelle) geometry. Peptides used here repeat a seven-amino acid sequence between one and four times to vary peptide length while maintaining similar peptide-peptide interactions. Without a hydrophobic tail, these peptides all exhibit a combination of random coil and α -helical structure. Upon self-assembly, however, short peptides are prone to β -sheet structure and cylindrical geometry while longer peptides remain helical in spheroidal micelles. The transition to β -sheets in short peptides is kinetic, whereby amphiphiles first self-assemble with helical peptide structure, then overcome an activation barrier as they transition to their equilibrium β -sheet structure at a rate that depends on both temperature and ionic strength. These results identify peptide length as an important control over equilibrium peptide secondary structure and micelle geometry. Furthermore, the kinetic nature of the helix-to-sheet transition opens the door for shape-changing bioinspired materials with tunable conversion rates.

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