

Random copolymers form crystalline structures with supramolecular polymers

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The ordering of polymer chains into well-defined crystal lattices remains a challenge due to kinetic barriers during crystallization and the difficult synthesis of structurally precise macromolecules. We report here on a strategy where monomers of a supramolecular polymer can be used to promote the crystallization of covalent polymers that lack the sequence and stereochemical control to crystallize on their own. Synchrotron X-ray scattering, absorbance spectroscopy, and coarse-grained molecular dynamics (CG-MD) simulations reveal that the supramolecular monomers co-crystallize with complementary motifs on the covalent polymer to form nanoscale structures under aqueous conditions. Transmission electron microscopy and CG-MD simulations show that this method can also be used to tune the size and shape of these nanostructures through a competition between the entropy of polymer chain folding and the formation enthalpy of an extended crystalline lattice. When these hybrid covalent-supramolecular polymers are used as photosensitizers in aqueous catalysis, we observe an unexpected enhancement in catalysis linked to their structure.

