Bio-Inspired Hierarchical Structure Formation in a Supramolecular Polymer

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Supramolecular polymers are based on discrete building blocks that thermoreversibly self-assemble into defined architectures through non-covalent interactions such as hydrogen bonding, often resulting in materials with tailored structure, dynamic behavior, properties and function. The attachment of supramolecular ligands to polymer chains is, however, almost exclusively restricted to low molecular weight polymer segments, which consequently lack entanglement and exhibit brittle failure under low loads in tension. We have developed a supramolecular modification strategy that persists even when high molecular weight base polymers are employed, which is based on the co-assembly of bioinspired oligopeptide end groups with a matching low molecular weight additive into highly dispersed, polymer-tethered nanofibrils. The resulting supramolecular network gives rise to a variety of new melt properties that promise drastic improvements in materials processability or recyclability, but a detailed structural characterization of these nanofibrils and a profound understanding of their formation is required for a universal applicability of this approach to various technologically important base polymers.

Here we investigate the structure formation behavior of a hydrophobic amorphous model polymer of three different molecular weights using the supramolecular approach aforementioned. We show that the hydrogen-bond-driven co-assembly of additives and end-groups result in a new phase which we were able to describe with a thermodynamic analytical model. This phase is composed of anti-parallel beta sheets, of which a defined number stack to form helical nanofibrils that, due to the self-limiting lateral aggregation thus have a defined and uniform diameter. As a result of the tethering and bridging of the nanofibrils with the attached polymer segments, they are periodically placed in an hexagonal arrangement in the bulk material.

