The University of Fribourg / Faculty of Sciences and Medicine / Department of Chemistry

Stimuli-Responsive Supramolecular Networks

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Supramolecular polymers (SPs) are formed by the self-assembly of monomeric units, which are connected through dynamic non-covalent interactions. The reversibility of these bonds can be exploited to disassemble SPs back into the monomeric species by application of external stimuli. Considering processing or recycling, this disassembly into monomeric species provides a distinct advantage over traditional covalent polymers. The response of SPs to appropriate stimuli is generally accompanied by drastic changes of macroscopic materials properties, potentially providing access to a wide range of useful responsive behaviors. However, the utility of stimuli-responsive SPs for applications has so far been limited by the low mechanical strength and stiffness of most of the reported examples. In this context, the present thesis aims to develop new macromolecular design concepts for supramolecular materials with robust mechanical properties and a (multi-) stimuli responsive behavior.

In the first part a highly cross-linked and semicrystalline SP network is reported, that self-assembles from a low-molecular weight trifunctional building block terminated with tridentate ligands and its complexes with Zn^{2+} ions. The material exhibits a high melting temperature, robust mechanical properties in the temperature range between the melting and glass transition temperature. At the same time, the stimuli-responsive properties such as optical healing and debond-on-demand adhesion are retained. The observed strength of this highly cross-linked structure is accompanied by a relatively low toughness, which considerably limits its resistance to fracture. In the second part of this work we will accordingly investigate the potential for a toughening of the developed robust and stiff supramolecular molecular network. In order to increase the ductility, we follow a strategy based on the incorporation of additional linear macromonomers, *i.e.*, a low glass transition end-functionalized telechelic with the same supramolecular motif which can co-assemble in the bulk. The mechanical properties of the blends were found to be tunable across a wide range as a function of the blend composition. The focus of the final part is the preparation and investigation of a multistimuli, multiresponsive polymer material. In this context, two supramolecular networks with the same trifunctional polymer core, but orthogonal non-covalent binding motifs (i.e., metal-ligand coordination and hydrogen bonding) will be combined within a single blend. The orthogonal nature of the interactions will allow for an independent disassembly of the metal-ligand complexes and hydrogen dimers by chemical and thermal stimuli.

Jury:

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