

Supramolecular polymer solids with orthogonal binding motifs

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Abstract

Supramolecular polymers (SPs) are formed by self-assembly of monomeric units that are connected by dynamic non-covalent interactions such as hydrogen bonding, metal-ligand coordination, ionic interactions, π - π stacking, or host-guest interactions. The reversibility of these bonds can be exploited to disassemble SPs back into their monomeric species, which can be achieved in a controlled manner by the application of specific stimuli including temperature, light or mechanical force. Most stimuli-responsive materials are based on a single type of supramolecular interaction; however, the combination of multiple (orthogonal) supramolecular interactions in one material in principle allows creating multi-responsive polymers, i.e., materials that respond to different stimuli with different property changes. While the orthogonality of a number of supramolecular binding motifs has been already demonstrated for several polymeric systems in solution,[1] very few reports have explored the potential of such interactions to create multi-responsive solid polymeric material.

Building on our group's recent work on supramolecular polymers with orthogonal functionalities,[2] we have synthesized two supramolecular macromonomers based on a telechelic trifunctional polypropylene oxide (PPO) core displaying either metal-coordinating 2,6-bis(1'-methylbenzimidazolyl)pyridine (Mebip) ligands or hydrogen-bonding ureipyrimidinone (UPy) units as end groups. This contribution will discuss the properties of the supramolecular networks obtained by assembly of the individual macromonomers via $(\text{Mebip})_2\text{Zn}^{2+}$ or UPy-UPy interactions and compare them with those of the mixed material (Figure 1), which can be regarded as two interpenetrated supramolecular networks. The orthogonality of the supramolecular interactions in the blended system will be discussed on the basis of UV-Vis analysis, small-angle X-ray scattering (SAXS) and dynamic mechanical thermal analysis (DMTA). The results show that the thermoresponsive behavior of these materials is driven mainly by the phase segregation of the binding motifs into well-defined hard phases that introduce physical cross-links. The two supramolecular networks appear to be co-continuous and can be sequentially and selectively disassembled upon increasing the temperature.

References

[1] Li, S.-L.; Xiao T.; Lin, C.; Wang, L. *Chem. Soc. Rev.*, **41** (2012) 5950-5968.

[2] Coulibaly, S.; Heinzmann, C.; Beyer, F. L.; Balog, S.; Weder, C.; Fiore, G. L. *Macromolecules*, **47** (2014) 8487-8496.

Figure

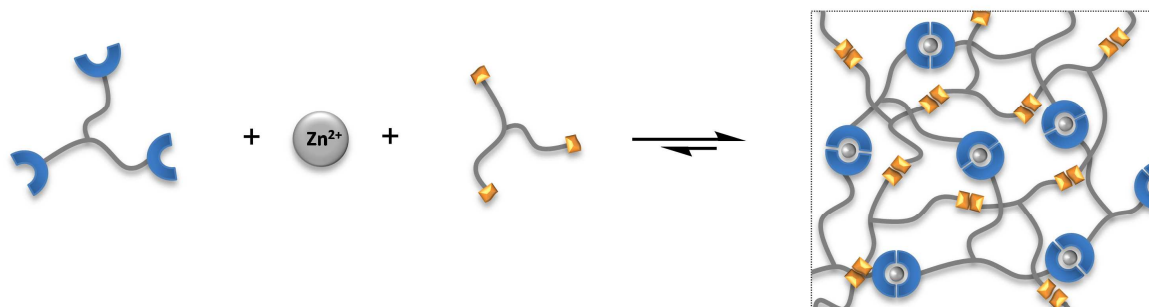


Figure 1. Schematic representation of orthogonal supramolecular binding upon mixing of two supramolecular macromonomers.