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Evolution of synthetic polymers into functional systems

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The development of precision polymer synthesis provides access to a broad library of abiotic structures, where monomers are placed in particular positions of macromolecule chains. Sequence-defined abiotic macromolecules are expected to exhibit folding, characteristic of biotic macromolecules and inherit similar functionalities. Control of abiotic macromolecule shape is a prerequisite to controlling their functionalities, as the secondary structure guides the performance of biomolecules. Here, I will discuss synthetic approaches leading to polyurethanes of discrete chemical structures with controlled monomer order and the impact of stereocontrol on their properties and functionalities. Using chiral monomers of different configurations, we can modulate the sequence of stereocenters in the backbone, which has consequences on chain mobility and self-assembly. Depending on the number of stereocenters, polyurethanes can fold into secondary structures. Interestingly, the attained shape can be tuned by the sequence of stereocenters. As a result, polyurethanes can organize into various shapes and self-assemblies according to chain stereoconfiguration. Changes in molecular interactions caused by stereorearrangements determine polyurethane functionalities. We evaluated the effect of stereochemistry on binding strength between model oligourethanes and a ligand. We found that stereocontrol significantly influences the structural properties of oligourethanes and the oligomer-ligand complexes leading to various dissociation constant values. We demonstrated that stereochemistry is emerging as an excellent tool for programming catalytic function of macromolecules. This discussion aims to shed light on the intricate relationship between sequence, stereocontrol and the properties of synthetic polymers, offering insights into their potential applications and relevance in mimicking biological systems by man-made laboratory evolution.