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Title: Stabilizing biologically relevant PPII structure of polyproline: Functionalization approach

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Abstract:

Functionalizable polymers pave the path for accessing more advanced and multifaceted synthetic materials. While advancement continues in this field, polymers with polyproline backbone are also growing as a favorable choice for the design of biomaterials. The distinctive structural arrangement of proline among amino acids arises from a five-membered pyrrolidine ring as the side chain and secondary amine in it. Thus, unlike other polypeptides the amide backbone of polyproline can induce both the cis and trans conformations. Moreover, a high energy barrier ~ 20 kcal/mole associated with the cis to trans isomerization ensure the stability of the both conformations independently. Owing to this high energy threshold, isomerization is not achievable under normal physiological conditions, but feasibility can be induced through modification in solvent, environment temperature, etc. Recent studies have already demonstrated the connection between the polyproline's structure with the isomerization and thermoresponsive behaviour. Thus, synthesizing a functionalizable polymer will serve the purpose of delivering polymers bearing tailored-made properties that can be fine-tuned for specific applications in the future. In this work, we synthesized clickable polyproline having propargyl moiety as the reactive handle for post-polymerization modifications. Our primary objective is to study the effect of periodically-grafted functional groups on the secondary structure of polyproline (PPI and PPII). Additionally, we also examine how thermoresponsive property get affected by the periodic functionalizations. The polymers were characterized using 1 H NMR and SEC analysis. The secondary structure of the polymers was characterized using CD spectroscopy. The thermal stability of the functionalized polyprolines were evaluated using turbidimetry and variable-temperature CD measurements. The post-polymerization modification of these polymers makes them a prospective choice for more exquisite applications in different fields and can be tailo

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