

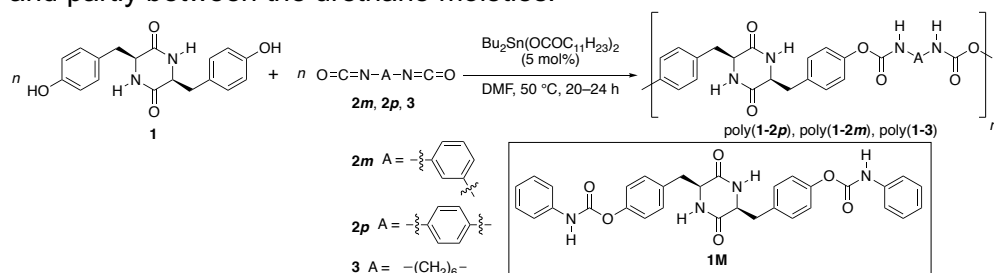
Diketopiperazine-Based Polyurethanes and Supramolecules. Mechanistic Aspects of Aggregation

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Diketopiperazine (DKP), an amino acid dimer, is the smallest cyclic peptide, which is known as a typical by-product in peptide synthesis. DKP has been mainly studied from a viewpoint of biology due to the physiological activity and enzyme inhibitory in a similar fashion to linear peptides. DKP consists of two *s-cis* amide groups capable of forming tandem hydrogen bonding strands in a parallel direction to the DKP ring, which makes DKP a promising building block for molecular assemblies. Meanwhile, polyurethane is a useful polymeric material widely used as adhesives, blowing agents, fibers, thermoplastic elastomers and coatings. The present study deals with the synthesis of polyurethanes by the polyaddition of L-tyrosine DKP and bifunctional diisocyanates, and examination on the aggregation behavior together with those of the model compound of the polymers.

The polyaddition of L-tyrosine DKP (**1**) with 1,3-phenylene diisocyanate (**2m**), 1,4-phenylene diisocyanate (**2p**) and hexamethylene diisocyanate (**3**) was carried out using Sn catalyst to obtain the corresponding polyurethanes poly(**1-2p**)–poly(**1-3**) having DKP moieties in the main chain (Scheme 1). Poly(**1-2p**) exhibited a negative circular dichroism (CD) signal assignable to the chirally arranged benzene rings, while poly(**1-2m**) and poly(**1-3**) did not exhibit such CD signal. Compound **1M** was synthesized as a model for the polymers. Interestingly, the viscosity of a solution of **1M** in THF gradually increased at room temperature, and the solution turned into the gel state after 5 hours, which was confirmed by dynamic viscoelasticity measurement. Fibrous patterns were observed by transmission electron and fluorescence microscopies. Dynamic light scattering, density functional theory calculations, and molecular dynamics simulations indicated the formation of aggregates based on intermolecular hydrogen bonding mainly between the DKP moieties and partly between the urethane moieties.



Scheme 1. Polyaddition of DKP **1** with diisocyanates **2m**, **2p** and **3**

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