



# The Physics of Soft and Biological Matter

## Kinetic control over out-of-equilibrium self-assembled hydrogels

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Self-assembly under thermodynamic control gives a well-defined single state due to minimizing the Gibb's free energy. In contrast, kinetic control over self-assembly processes allows us to access many different states of a system. However, our limited understanding of the kinetics of self-assembly process restricts our ability to design kinetically controlled self-assembly routes. Here we explore a new method to kinetically control multi-step self-assembly using dynamic combinatorial chemistry. The first step starts with a dynamic combinatorial library of macrocycles functionalised with different numbers of peptide side-groups. The macrocycles are held together by reversible disulfide covalent bonds. Then the peptides start to interact to assemble macrocycles into fibres, which form a hydrogel. We tune the physical properties of the hydrogel using various methods such as photo-irradiation, adding cross-linker and varying salt concentration. We relate the gel properties to their structure by performing rheology measurement and direct visualization techniques including Cryo-TEM and AFM. Our results suggest that, on one hand, photo-irradiation initiates a reshuffling of the disulfide bonds within the fibres, causing the fibres to be less fragile and including gelation through entanglement of the fibres. On the other hand, adding cross-linker or varying salt can enhance the gel strength significantly. These results open up new possibilities in the kinetic control of self-assembly process.