Biobased and pH-responsive Supramacromolecular Microgels with tunable size and shape via droplet-based Microfluidics

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Among the plethora of polymer networks, microgels have raised strong interest in many scientific areas. These colloidal polymer networks show a controlled responsive behavior, high stability, and bio-compatibility.^[1] Introducing supramolecular functionalities into microgels enables the degradation *via* stimuli such as light, redox, or pH, which can be used to release drugs or control their physicochemical properties on-demand.^[2] The aim of the present study is to design aqueous microgels based on supramolecular cross-links via droplet-based microfluidics.^[3] The natural polyphenol tannic acid (TA) is used as a physical cross-linker which enables hydrogen bonding with the carbonyl group of the poly(N-vinylcaprolactam) (PVCL) chain. We synthesized a series of microgels at a fixed pre-polymer PVCL concentration with a variable content of tannic acid. All synthesized microgels are stable in water and could be cleaved instantly with increasing pH by the addition of aqueous NaOH, which breaks hydrogen bonding. Evidence shows also that microgels deswell at low pH in the presence of an HCL solution, which is believed to be due to the increasing amount of hydrogen bonding between the polymer chain and the cross-linker. Introducing a new type of design of the microfluidic chip enables on-chip gelation. With this setup, we could control of gelation process and fabricate rod-shaped microgels with tunable aspect ratios. Using self-assembly of PVCL nanogels at interfaces and by interlocking them, we could also achieve colloidosomes. Furthermore, a model system for encapsulation and release of colloidal small PVCL microgel particles (1.2 µm) tagged with FITC dye could be demonstrated. This work clearly shows that the pHresponsive microgels have the potential to load/release various bioactives such as drugs, bacteria, cells, or other bio-reagents.

Keywords: Supramacromolecular microgels, Rod-shaped microgels, Tannic acid, Microfluidics



Figure 1. Fabrication of supramacromolecular microgels with tunable shape via microfluidics.[3]

References

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