Small but Smart: Sensitive and Supramolecular Microgels

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"Smart" microgels are micrometer-sized polymer gel particles that react to external stimuli, either by selective swelling and deswelling or by triggered crosslinking and decrosslinking.¹ The first class of response is achieved through the use of microgels that are composed of polymers with sensitive solubility,² whereas the second class of response is realized by reversible supramolecular polymer crosslinking rather than permanent chemical crosslinking.³ Both classes of response are attractive for practical applications; they are also useful in fundamental research, where microgels serve to build and investigate complex soft matter.⁴

A powerful approach to fabricate smart microgels with exquisite control is through the use of droplet-based microfluidic templating.¹ The idea of this approach is to use emulsion droplets as templates for the particle synthesis and to control the size, shape, and monodispersity of the microgels by controlling that of the pre-microgel droplets. Combination of this approach with the use of functional, macromolecular precursors, allows the polymer synthesis and the particle gelation to be controlled independently.⁵ This approach also allows complex particle morphologies such as hollow,⁵ anisotropic,⁶ or multi-layered^{7,8} microgels to be formed and complexed with additives, including living cells.⁹ Such microgels are particularly useful in encapsulation and controlled release applications.^{7,10}

In addition to their utility for encapsulation, responsive microgels can serve as model colloids to study the mechanics and dynamics of soft matter. For example, this approach allows exploring how nanostructural inhomogeneities affect the properties of sensitive polymer gels. To study this effect, droplet-based microfluidics can be used to fabricate micrometer-sized gel particles that are complexed with a precisely controlled degree of internal inhomogeneities, offering the possibility to study their impact.¹¹ A particularly powerful strategy is to combine droplet-based microfludics and small-angle x-ray scattering.¹² In addition, microgels can be used as building blocks to create larger soft materials, providing another means of purposely creating inhomogeneous composite systems to be studied.¹³ With these approaches, fundamental understanding on the effect and evolution of nanostructural complexity in sensitive gels can employed in rational design of advanced soft materials. In combination, both the upper directions of research therefore allow sensitive and supramolecular microgels to be tailored for various applications as multifunctional materials.

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