Controlling the structure of star-like copolymer microgels through the monomer chain length to modulate softness and deswelling

Jacopo Vialetto a,b, Megha Emerse a, Gavino Bassu a,b, Jürgen Allgaier c, Marco Laurati a,b

a Department of Chemistry, University of Florence, via della Lastruccia 3, Sesto Fiorentino, I-50019 Firenze, Italy.
b Consorzio interuniversitario per lo sviluppo dei Sistemi a Grande Interfase (CSGI), via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy.
c Jülich Centre for Neutron Science (JCNS), Forschungszentrum Jülich GmbH, Wilhelm-Johnen-Straße, 52428 Jülich, Germany.

jacopo.vialetto@unifi.it

Softness and stimulus responsivity of deformable polymeric particles are at the core of their properties and behaviors in suspension or when interacting with interfaces, being thus fundamental parameters for the design of functional materials and complex fluids. Synthetic microgels, crosslinked polymeric networks partially soluble in the solvent in which they are dispersed, particular those made of poly(N-isopropylacrylamide) (PNIPAM), are one of the most prominent example of soft colloids, and are extensively studied for fundamental understanding of soft matter systems and for their application potential.
We recently discovered,[1] combining experiments and monomer-resolved simulations, that replacing commonly used crosslinkers with ethylene glycol dimethacrylate (EGDMA) allows obtaining microgels with an unprecedented internal structure combining microgel features with that of star polymers. Such a star-like morphology presents a small and dense core containing most of EGDMA and a sparse shell with polymer arms, particularly at low crosslinker concentration. These star-like microgels fully retain PNIPAM thermoresponsivity and undergo a sharp volume phase transition at ~32 °C.
Taking a step further, in this presentation I will show that copolymerization with oligo(ethylene-glycol) methyl-ether-methacrylates (OEGMA) of varying chain lengths represents a powerful handle to control particle softness and thermal response.[2] Light and neutron scattering allowed us to quantify the single-particle bulk modulus and link it to temperature-induced deswelling, elucidating the complex interplay between network conformation and mechanical properties in response to different stimuli. The results reveal a non-trivial dependence on comonomer chain length: short OEGMA chains smooth the core–shell contrast yielding more homogeneous particles, while longer chains produce extremely compliant star-like morphologies that maintain star features even at high temperature. Overall, these findings provide new tools to finely tune softness and stimulus responsivity of soft colloids.

References:

[1] Ballin et al., ACS Nano 2025, 19, 35447.
[2] Vialetto et al., JCIS 2026, 703, 139162.