Block-like monomer distribution and heterogeneous collapse of thermoresponsive copolymer microgels

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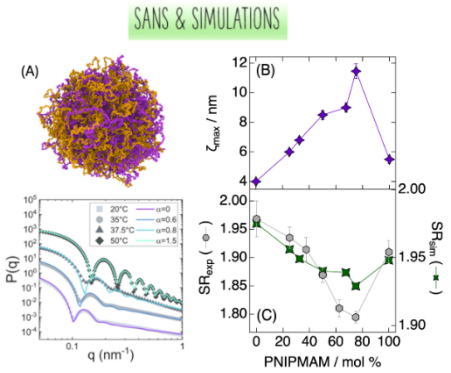
The internal structure of microgels is fundamental in determining their responsiveness and thus potential applications. It remains however difficult to resolve with molecular resolution. In this work we combine small-angle neutron scattering (SANS), dynamic light scattering (DLS), and nuclear magnetic resonance (NMR) measurements with multi-scale simulations to investigate the internal structure of Poly(N-isopropylacrylamide-co-N isopropylmethacrylamide), P(NIPAM-co-NIPMAM), copolymer microgels, in which a random monomer distribution is conventionally assumed. By synthesizing samples containing selectively deuterated PNIPAM or PNIPMAM we probe the individual distributions of these components that we compare with simulation results obtained for different copolymer models (Fig.1 A). In particular, direct comparison between experimental and numerical form factors provides evidence of preferential organization into block structures, challenging the prevailing view of random distribution. Additional 13C-NMR experiments confirm NIPAM-rich blocks and atomistic simulations provide a link between this unexpected block-like architecture and distinct local hydrogen-bonding patterns.
SANS analysis also reveals for all investigated copolymer compositions a maximum in the polymer mesh correlation length near the volume phase transition, evidencing coexistence of collapsed NIPAM-rich and swollen domains (Fig.1 B). The correlation length increases with increasing NIPMAM content, reaching a maximum at 75 mol % NIPMAM, implying a large degree of heterogeneity due to the presence of a large fraction of intercalated, non-collapsing PNIPMAM monomers. The maximum heterogeneity corresponds to a minimum in the equilibrium swelling ratio (Fig.1 C), suggesting that collapsed microgels retain a structural memory of the transition and present a less-compliant structure in response to temperature variations. Overall, these insights highlight a complex effect of the block-like monomer distribution on the responsive properties of copolymer microgels with different compositions, thus providing a design rule for tailoring responsive colloids for functional soft materials.



(A) Simulation snapshot of a 50:50 PNIPAM-PNIPMAM microgel and simulation-SANS comparison at different temperatures. (B) Maximal correlation length and (C) swelling ratio (experimental and simulated) as a function of composition.

References:

[1] Letizia Tavagnacco. Elena Buratti. Jacopo Vialetto et al. Small 21, 47, e09795. 2025. [2] Jacopo Vialetto, Francesco Brasili, Letizia Tavagnacco et al. In preparation. 2025.