

Controlling the volume phase transition and structure of microgels by copolymerization

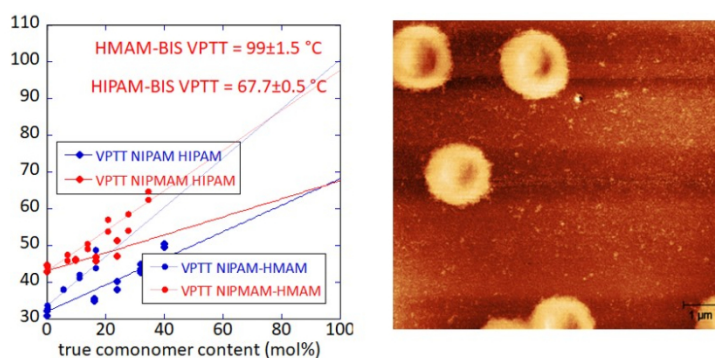
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The thermosensitivity of microgel particles, i.e. their temperature-dependent swelling properties, has triggered ongoing interest over the past forty years. The most-studied family of polymers is represented by poly(N-isopropylacrylamide), PNIPAM. Here, we aim at controlling the microgel VPTT by copolymerization with comonomers of different hydrophilicity, for energy applications. We precisely determine the incorporation of N-(hydroxymethyl)acrylamide (HMAM) and purpose-synthesized N-(2-hydroxyisopropyl)acrylamide (HIPAM) and N-(1-hydroxy-2-propyl)methacrylamide (NIPMAMol) into microgels. The swelling properties and microstructure of the resulting copolymer microgels are then characterized via turbidimetry, DLS, SANS, and AFM. At low comonomer contents, all microgel particles exhibit moderate growth in size. Beyond a threshold, we observe a significant jump in size, and smoother swelling behavior. For NIPAM-HIPAM, the size increase is linked to a strong rise in swelling capacity, and the formation of a thick corona. The effect of the hydrophilic comonomers on the VPTT correlates linearly with their true composition, allowing us to extrapolate the VPTT of hypothetical pure comonomer microgels. This leads to ca. 99°C for HMAM, 85°C for NIPMAMol, and 68°C for HIPAM for the respective VPTT, indicating their effect on the VPTT in the copolymerized microgels. The observed changes in VPTT, swelling, size, and morphology suggest that high-VPTT microgels possess unique internal molecular composition gradients, likely due to hydrophobic interactions during synthesis.



Left) VPTTs of copolymer microgels with extrapolation to pure comonomer microgels. Right) Observation of nominal 50 mol% NIPAM-HIPAM microgels in the dry state by AFM.

References:

Smart Copolymer Microgels with High Volume Phase Transition Temperatures: Composition, Swelling, and Morphology, Aditi Gujare, Stefanie Uredat, Jonas Runge, Felix Morgenstern, Domenico Truzzolillo, Thomas Hellweg*, and Julian Oberdisse*, *Langmuir* 2025, 41, 45, 30442-3045