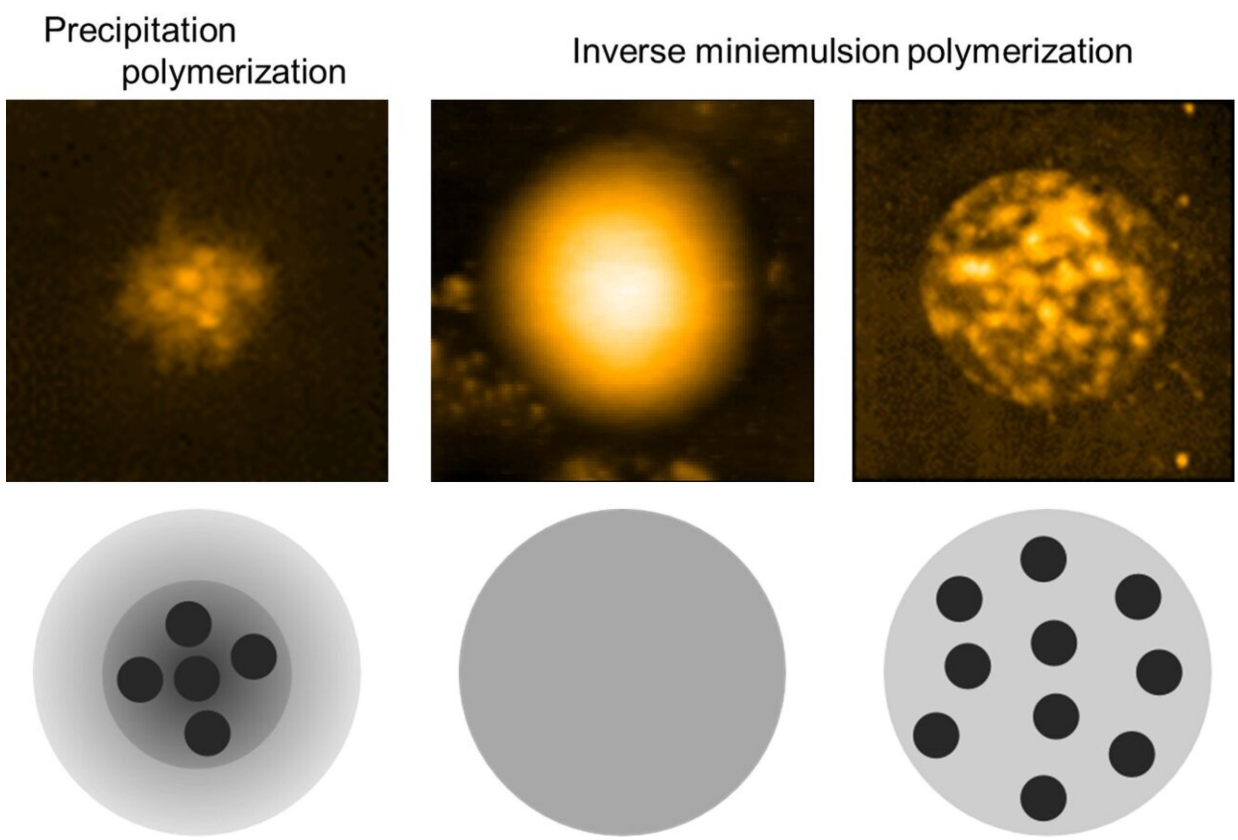
Uncovering microgel mysteries

May 30 2019



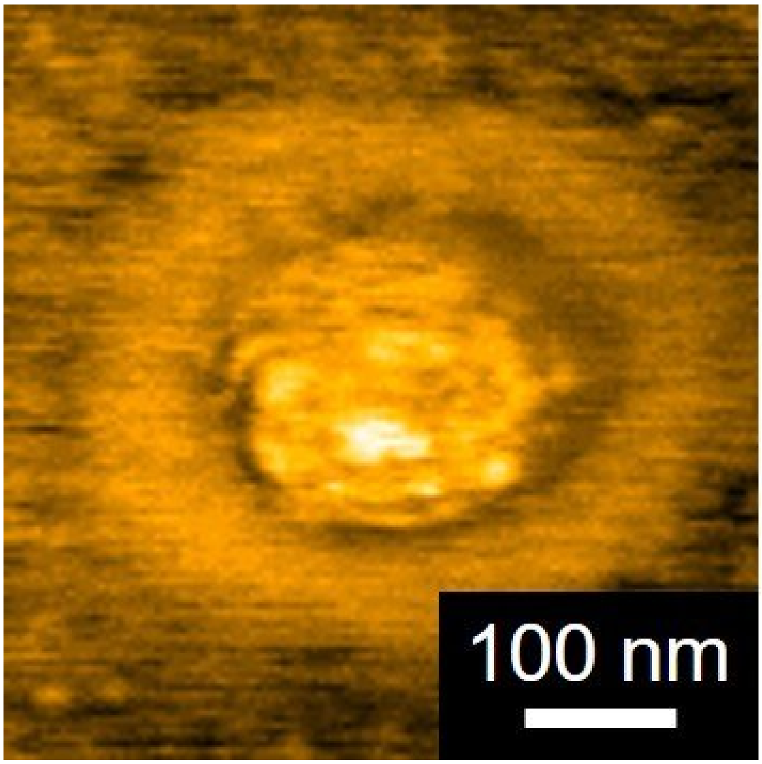
TC HS AFM analysis of microgels synthesized by different polymerization techniques: (left) precipitation polymerization, (center) inverse miniemulsion polymerization below the VPTT, and (right) inverse miniemulsion polymetization above the VPTT. Credit: Nishizawa *et al.*, *Angewandte Chemie International Edition*, 2019, Wiley-VCH Verlag GmbH & Co. KGaA

Researchers at Shinshu University successfully recorded previously unexplained behavior of hydrogel microspheres (microgels) using a newly customized tool: temperature-controlled high-speed atomic force microscopy (TC HS AFM). This machine, which is the only one in the world, was assembled by Dr. Takayuki Uchihashi of Nagoya University to investigate proteins. It was applied for the first time to the study of microgels by the team at Daisuke Suzuki Laboratory, Graduate School of Textile Science & Technology and RISM (Research Initiative for Supra-Materials) of Shinshu University. The study lead by first year doctoral candidate, Yuichiro Nishizawa, succeeded in observing the structure of the microgels which had been difficult due to limitations of previous equipment.

The structure of microgels has been studied extensively using scattering and imaging techniques including electron microscopy, fluorescence microscopy, atomic force microscopy, and super-resolution microscopy. The thermoresponsive properties of the core-shell structures had been well documented using such techniques. Using TC HS AFM, they were able to observe and record the particles in detail, non-thermoresponsive inhomogeneous decanano-scale spherical domains, which had been hypothesized by Dr. Kenji Urayama of the Kyoto Institute of Technology.

Nishizawa states, "as our research indicated, hydrogel microspheres have heterogeneous structure in almost every case. Moreover, the heterogeneous nano structure would have an impact on the physicochemical properties of water swollen microgels and would lead to a gap between theory and result. We believe that our findings can contribute to the understanding of these gaps."

The Shinshu University team first studied the microgels synthesized by precipitation polymerization. This gel has the core-shell structure, as well as non-thermoresponsive spherical domains. Using inverse miniemulsion polymerization techniques, they were able to produce two more types of microgels previously thought to all be the same, but which were observed to behave differently.



Phase image of a magnified NB10 microgel at 40.3 °C. Although domains could not be defined using the height images, they were observed in the phase images. Therefore, it seems likely that the domains are embedded in the core region of the highly crosslinked microgels. Credit: Nishizawa *et al*., *Angewandte Chemie International Edition*, 2019, Wiley-VCH Verlag GmbH & Co. KGaA

Microgels made by inverse miniemulsion polymerization below the VPTT produced a gel that did not have the non-thermoresponsive domain, nor did it have the classic core-shell structure—it was uniformly homogenous. A third method, using the inverse miniemulsion polymerization above the VPTT produced an inhomogeonous gel with no core-shell structure, but with nano- to submicron-sized non-thermoresponsive domains. The Shinshu team were able to show that the method of production greatly effects the differences in the structure and therefore behavior of the three types of microgels.

This study provides insight into all thermoresponsive microgels and perhaps other stimuli-responsive colloids. The knowledge that the method of production has a strong effect on the structure will help develop real world applications such as microgel glass/crystal and other medical materials. The Shinshu team hope to continue the study of hydrogel microspheres. Nishizawa says, "ultimately, we want to develop new types of microspheres which improve people's standard of living."

More information: Yuichiro Nishizawa et al, Non-Thermoresponsive Decanano-sized Domains in Thermoresponsive Hydrogel Microspheres Revealed by Temperature-Controlled High-Speed Atomic Force Microscopy, *Angewandte Chemie International Edition* (2019). DOI: 10.1002/anie.201903483

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