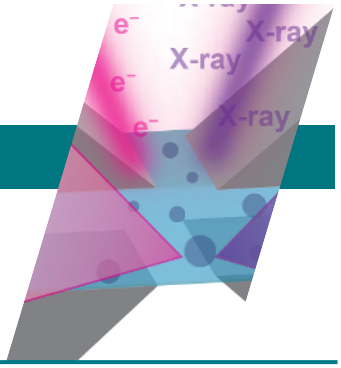
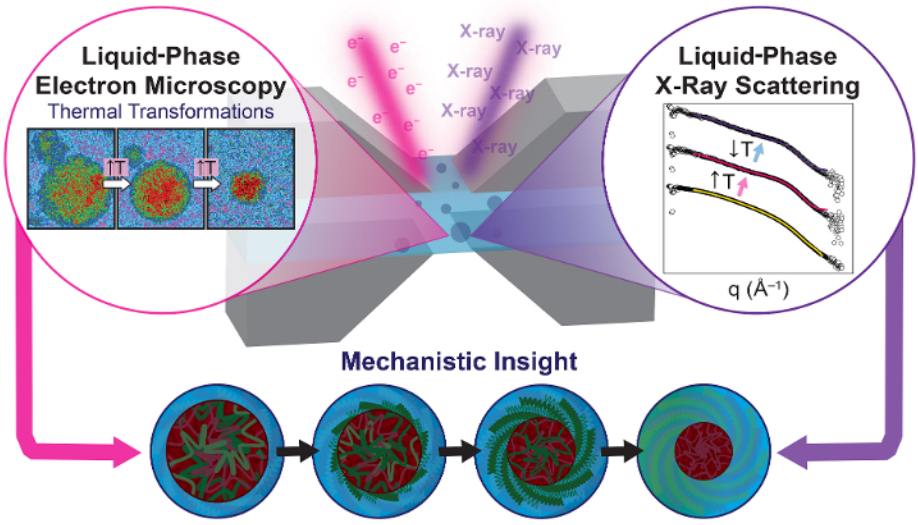



MATERIALS SCIENCES

# Insight into How Thermoresponive Nanomaterials Work




To study what happens in a thermally responsive nanomaterial made up of polymers in solution, researchers used a multimodal approach that combined liquid-phase electron microscopy and resonant soft x-ray scattering.

## Scientific Achievement

By combining soft x-ray scattering at the Advanced Light Source (ALS) with electron microscopy, researchers learned how nanoscale polymer assemblies in solution restructure in response to heating.

## Significance and Impact

The approach can be generalized to many complex, solution-phase, nanoscale processes, and holds promise for driving advances in applications from drug delivery to catalysis.

## Unraveling "smart" polymers

Some materials have properties that change (such as color, conductivity, or shape) in response to relatively small changes in environmental conditions (such as humidity, light, or temperature). This category of highly responsive, "smart" materials includes block copolymers, which consist of two or more types of monomer chains that self-assemble into discrete regions (or "blocks"). In blocks with both hydrophilic (water-loving) and hydrophobic (water-avoiding) components, heating to a critical temperature can weaken interactions between monomers in favor of interactions with the solvent, thus triggering nanoscale restructuring that can affect the material's overall physical properties. Scientists would like to leverage the dynamic behavior of such temperature-responsive polymers for numerous applications, ranging from drug delivery to catalysis.

To gain mechanistic insight into the solution-phase dynamics of these polymers, a team of researchers coupled liquid-phase electron microscopy with liquid-phase variable-temperature resonant soft x-ray scattering (VT-RSoXS). Correlating the data obtained from using the techniques in tandem provided a powerful approach to understanding complex nanoscale dynamics in solution.

## Directly visualizing nanoscale transformations

Despite the potential utility of temperature-responsive polymeric nanomaterials, their thermal phase transformations cannot be captured by standard microscopy methods that rely on static imaging of dried or cryogenically vitrified samples. Moreover, even liquid-phase x-ray scattering methods present a challenge, as appropriate model selection for data fitting is nontrivial and is often guided by electron microscopy, which is not optimized for non-aqueous solvents such as isopropyl alcohol, commonly used for these samples.

Variable-temperature liquid-cell transmission electron microscopy (VT-LCTEM) can directly visualize solvated nanostructures at different temperatures. A VT-LCTEM platform at Northwestern University's NUANCE Center utilizes two microchips that sandwich together a liquid sample, enabling observation under high vacuum. The researchers used this apparatus to trigger and observe thermal transformations of a block copolymer nanomaterial designed with a temperature-sensitive block. Notably, the

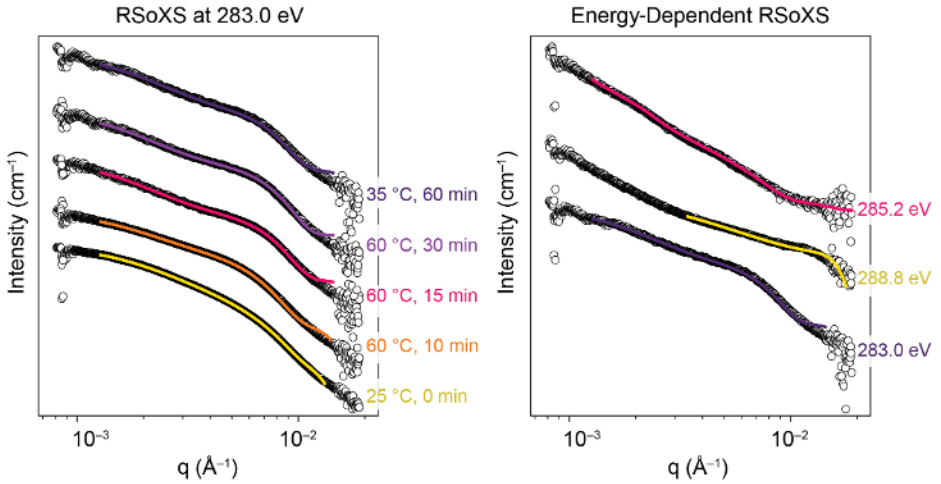
nanostructures were observed to shrink upon heating, transitioning from complex, multiphase core-shell particles to increasingly uniform particles.

## Correlation with soft x-ray scattering

To more rigorously characterize the transformation, the researchers turned to VT-RSoXS at ALS Beamline 11.0.1.2, which utilizes a novel liquid cell with a sample geometry identical to that of the VT-LCTEM platform. It provides complementary data about periodicity and order, collected under the same experimental conditions. Critically, liquid RSoXS is capable of probing complex, multicomponent polymeric nanoarchitectures because the scattering intensity is sensitive to the differing compositions of various regions, a feature that proved essential for probing the multiblock copolymer studied in this work.

Using VT-RSoXS, the researchers analyzed the individual blocks within the multiblock copolymer and determined that the particle shrinking observed by VT-LCTEM represented a morphological transition from polydisperse core-shell structures with multiphase cores to more-ordered spherical micelles. Moreover, the researchers probed the final kinetically trapped morphology formed upon cooling the sample. By leveraging VT-RSoXS and VT-LCTEM in tandem, the authors proposed a mechanism for the thermally triggered polymer transformation that could not be confidently assigned by using either scattering or electron microscopy in isolation.

Study co-authors Joanna Korpanty, Cheng Wang, and Nathan Gianneschi.




**Left: RSoXS data measured at 283.0 eV as the sample was heated and cooled over the course of one hour. Open circles are data points, and colored lines are model fits. The broad trace at room temperature (25 °C) is indicative of the high polydispersity of the initial assemblies. Upon heating for 10 minutes, a scattering feature (a kink in the curve) appeared at q ~ 0.007 $nm^{-1}$, suggesting greater ordering of the polymer nanoassemblies and a decrease in the size of the particle cores. Upon cooling to below 35 °C, the model fit indicates that the transformation is partially reversible. Right: RSoXS data measured upon cooling the sample and holding it at room temperature for 30 minutes. Additional energies (285.2 eV and 288.8 eV) were used to probe different aspects of the final particle morphology.**

In the future, the researchers hope to use their generalizable workflow, combining liquid-phase electron microscopy with resonant soft x-ray scattering, to answer fundamental questions about functional and responsive nanomaterials of all kinds.

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**Publications:** J. Korpanty and N.C. Gianneschi (Northwestern University) and C. Wang (ALS).

**Researchers:** J. Korpanty, C. Wang, and N.C. Gianneschi, "Upper Critical Solution Temperature Polymer Assemblies via Variable Temperature Liquid Phase Transmission Electron Microscopy and Liquid Resonant Soft X-Ray Scattering," *Nat. Commun.* **14**, 3441 (2023); doi:10.1038/s41467-023-38781-2.

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