

# Nanostructure Formation Behavior of Branched Poly(*N*-isopropylacrylamide)s in Water

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The thermoresponsive behavior of star-branched poly(*N*-isopropylacrylamide) (sPNIPAM) in an aqueous solution has been investigated using synchrotron-radiation small angle X-ray scattering (SAXS) and electrophoretic light scattering. The temperature-induced formation of spherical nanoparticles with narrow size distribution in sPNIPAM solutions at different temperatures (15 - 55°C) was investigated. The samples contained different end groups: carboxyl, hydroxyl, and benzyl. Unlike linear PNIPAM, sPNIPAM solutions remained transparent even at high temperatures, above the phase separation temperature of linear PNIPAM.

At elevated temperatures (45 °C and above), the formation of nano-sized spherical particles with aggregation numbers between 10 and 50 was observed, regardless of the end group. The stability of these particles was attributed to electrostatic repulsion, as indicated by the negative  $\zeta$  potential measured at high temperatures. Interestingly, this stability was reduced in the presence of NaCl, resulting in turbidity of the solution.

Comparative studies between constant and rapid heating processes showed that rapid heating resulted in more uniform nanoparticle formation, probably due to spinodal decomposition, a dominant mechanism under such rapid heating conditions (Figure 1). This process produced narrower size distributions compared to constant heating. The resulting internal polymer mass concentrations ( $c_{in}$ ) of the nanoparticles were calculated to be between 0.14 and 0.36 g cm<sup>-3</sup>.

These results suggest that the star-shaped structure of sPNIPAM plays a critical role in temperature-induced nanoparticle formation, providing a method for controlled nanoparticle fabrication. Similar behaviors have recently been observed for comb-branched PNIPAM and star-like PNIPAM micelles. We will also present our recent results on the nanoparticle formation behavior of these polymers.

## References

[1] K. Terao *et al.*, *Macromolecules*, **56**, 5635–5641 (2023).

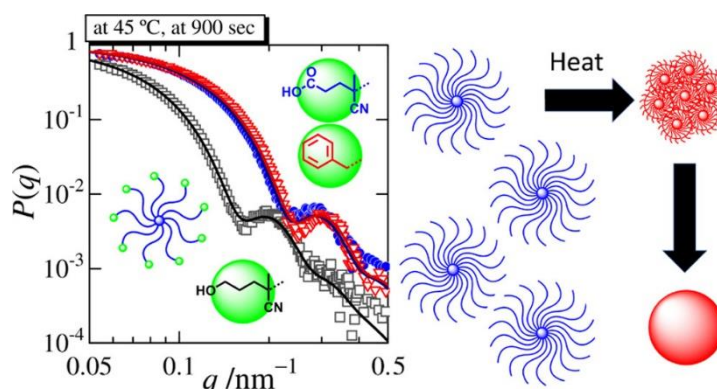


Figure 1. Double logarithmic plots of the form factor  $P(q)$  of sPNIPAM in water after rapidly heated in water and schematic representation of formation of nanoparticles from star branched polymer in water.