Towards Optimizing Synthesis Temperature for Microgels with Large Degree of Deswelling

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Abstract

Polysaccharide microgels have been synthesized at various temperatures (Tsyn) above the LCST of the parent polymer. Microgel structure and dynamics below and above the corresponding volume phase transition has been studied with light scattering. All microgels were found to undergo a reversible 15-50-fold deswelling in volume. However, the size distribution, structure, dynamics, and deswelling ability of microgels were found to strongly depend on synthesis temperature. In this work, the attempt was made to optimize the synthesis temperature to yield more monodisperse microgels with a larger degree of deswelling and to understand the role of the Tsyn on the density of microgels.
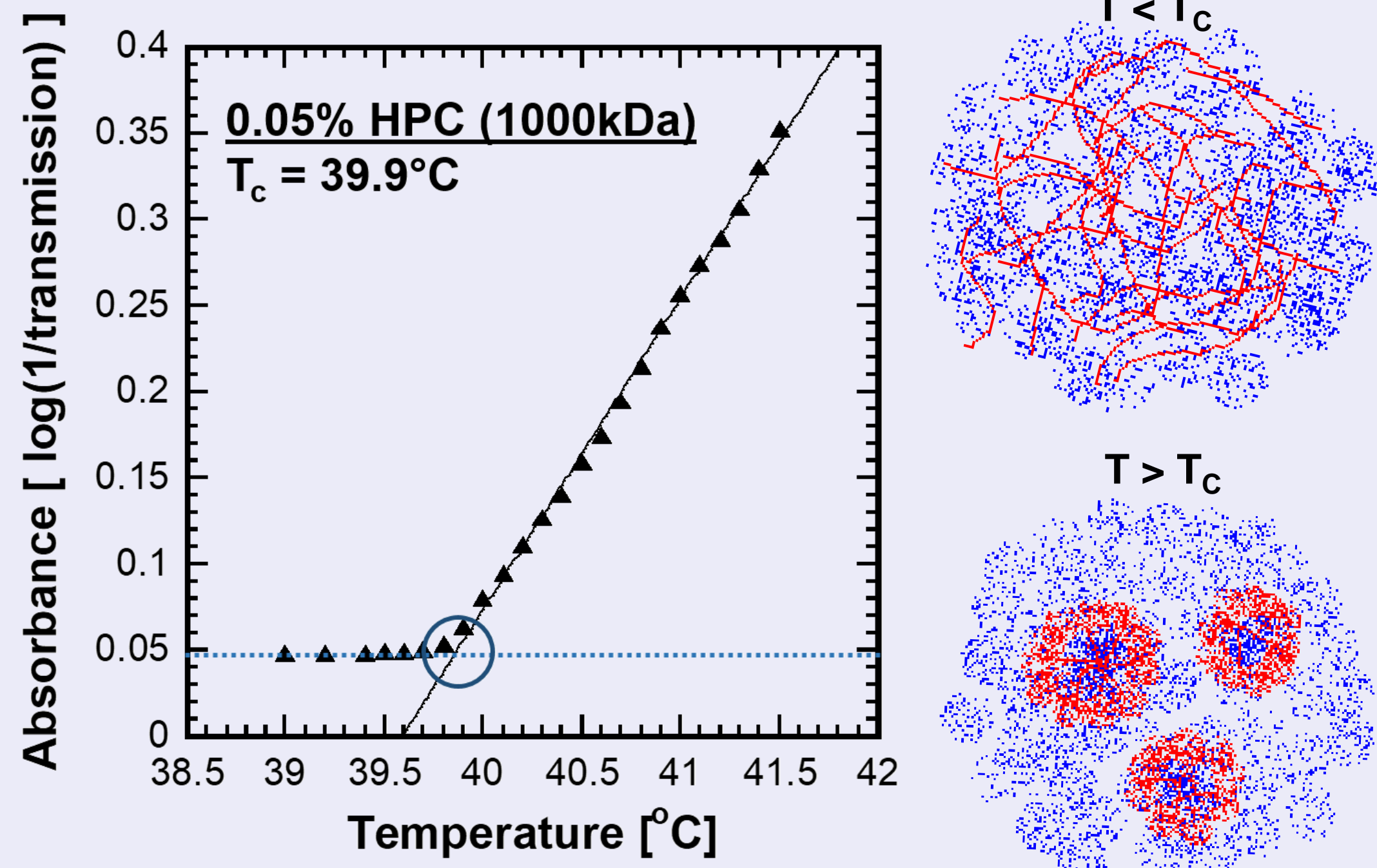
Polysaccharide Microgels

☐ **Microgels** are gel clusters formed by the chemical crosslinking of polymer chains

☐ We synthesized microgels with **hydroxypropylcellulose (HPC), an FDA-approved amphiphilic polysaccharide**

☐ Since microgels **inherit the properties of their parent polymer**, our particles exhibit a volume phase transition at high temperatures

☐ Due to their environmental responsivity and low toxicity, our microgels have potential to be used in **biomedical applications** including targeted drug delivery
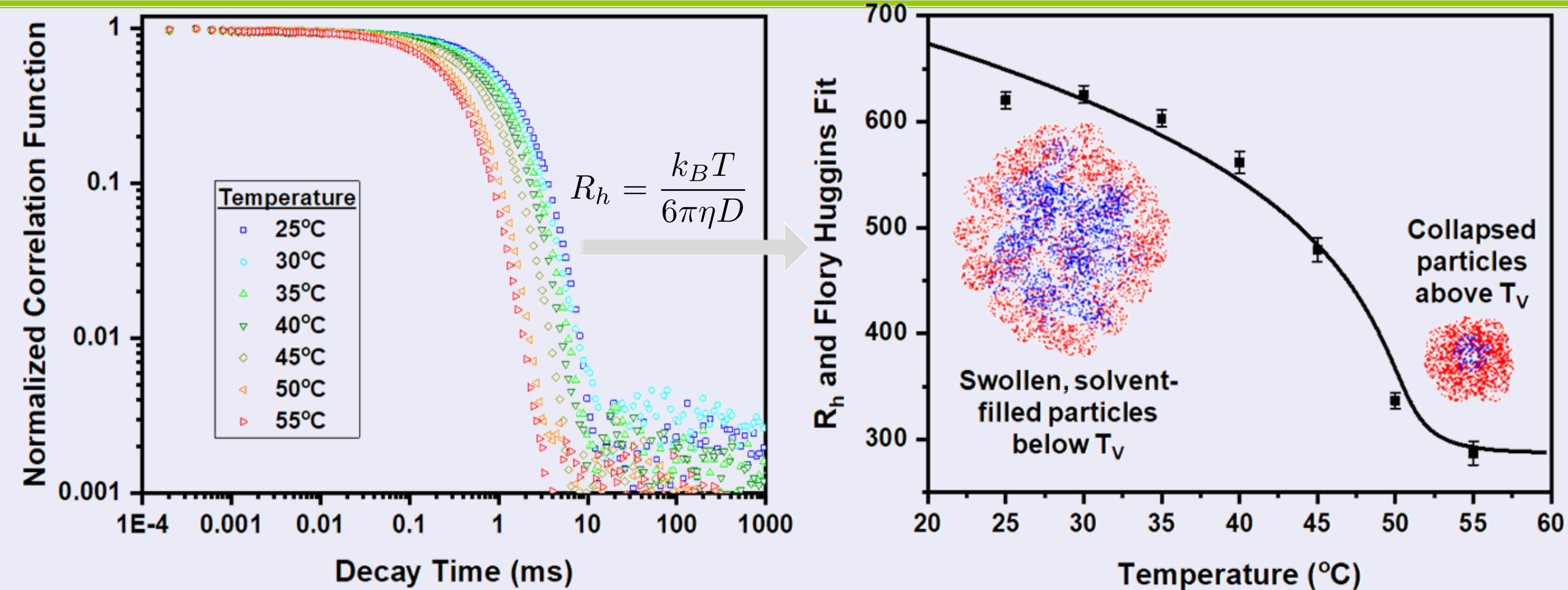
Parent polymer and synthesized microgel particles

Hydroxypropyl Celluose

• Naturally occurring 1MDa polysaccharide which is electrically neutral, rigid, and rodlike

• Amphiphilic nature leads to polymer dewetting transition at $T_C \approx 40°C$

• Crosslinking polymer chains at $T_{syn} > T_C$ forms sponge-like microgel particles that undergo a volume phase transition at T_v


0.05% HPC (1000kDa)
$T_c = 39.9°C$

$T < T_C$

$T > T_C$

Modelling particle shrinkage with Flory Huggins

$$R_h = \frac{k_B T}{6\pi \eta D}$$

Collapsed particles above T_V

Swollen, solvent-filled particles below T_V

Flory Huggins Mean Field Theory[1]:

$$T = \frac{\Delta H}{k_B \left[\frac{v_1 v}{N_A \phi^2} \left[\left(\frac{\phi}{\phi_0} \right) - 2 \left(\frac{\phi}{\phi_0} \right)^{1/3} \right] - \frac{2}{\phi} - \frac{2\ln(1-\phi)}{\phi^2} \right] + \Delta S}$$

$$\phi(T) = \left(\frac{R_{min}}{R_h} \right)^3$$

• In agreement with the literature[2,3], we found that fixing one parameter in the Flory Huggins model produced better (more stable, more consistent) fits to the experimental data

• To study the effect of $\Delta T = T_{syn} - T_C$ on particle density, ν, we opted to fix either ΔH or ΔS
  • Since the ratio $\Delta H / \Delta S$ is a close approximation[3] of the constant volume phase transition temperature, T_V, the choice of fixing either ΔH or ΔS is inconsequential. We chose ΔS.

• Fitting shrinkage curves with the Flory Huggins model yields three important results:
  • dH/dS approximation of T_V • Maximum slope measure of T_V • Particle density, ν
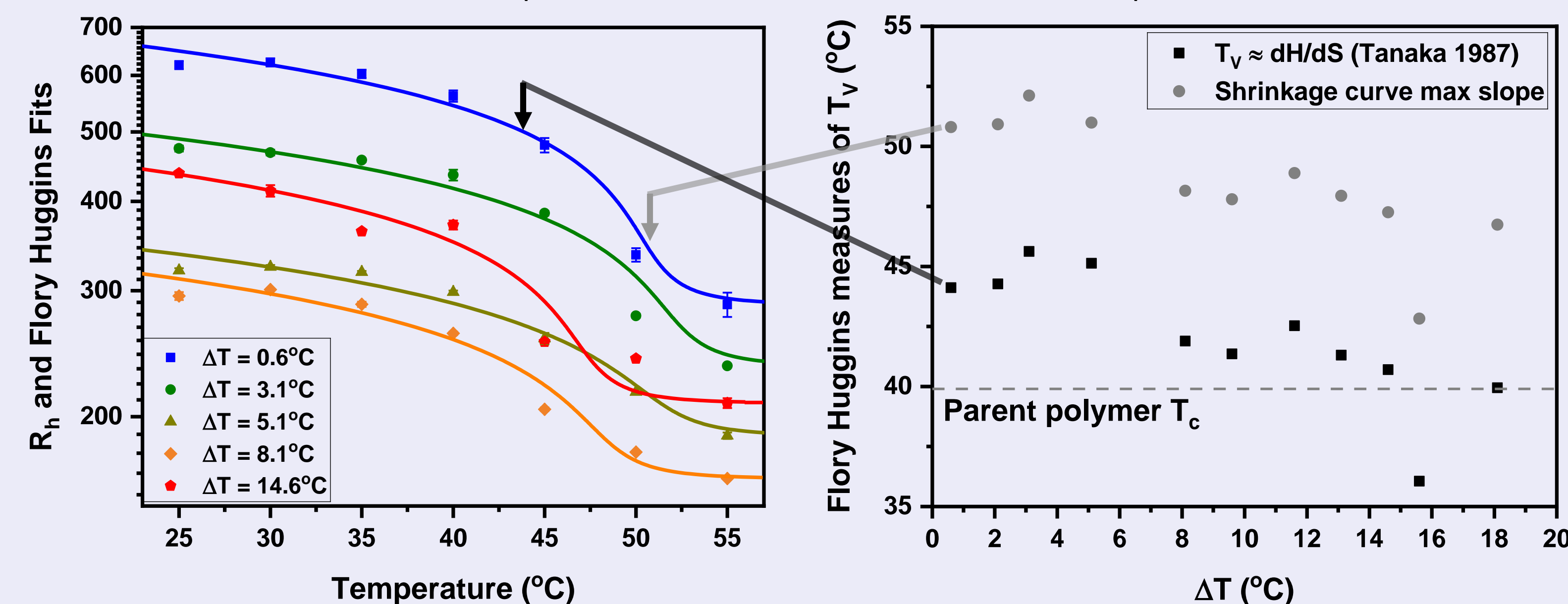

Using SLS and DLS to explore the effect of T_{syn} on:

1) Particle size and swelling/loading capacity
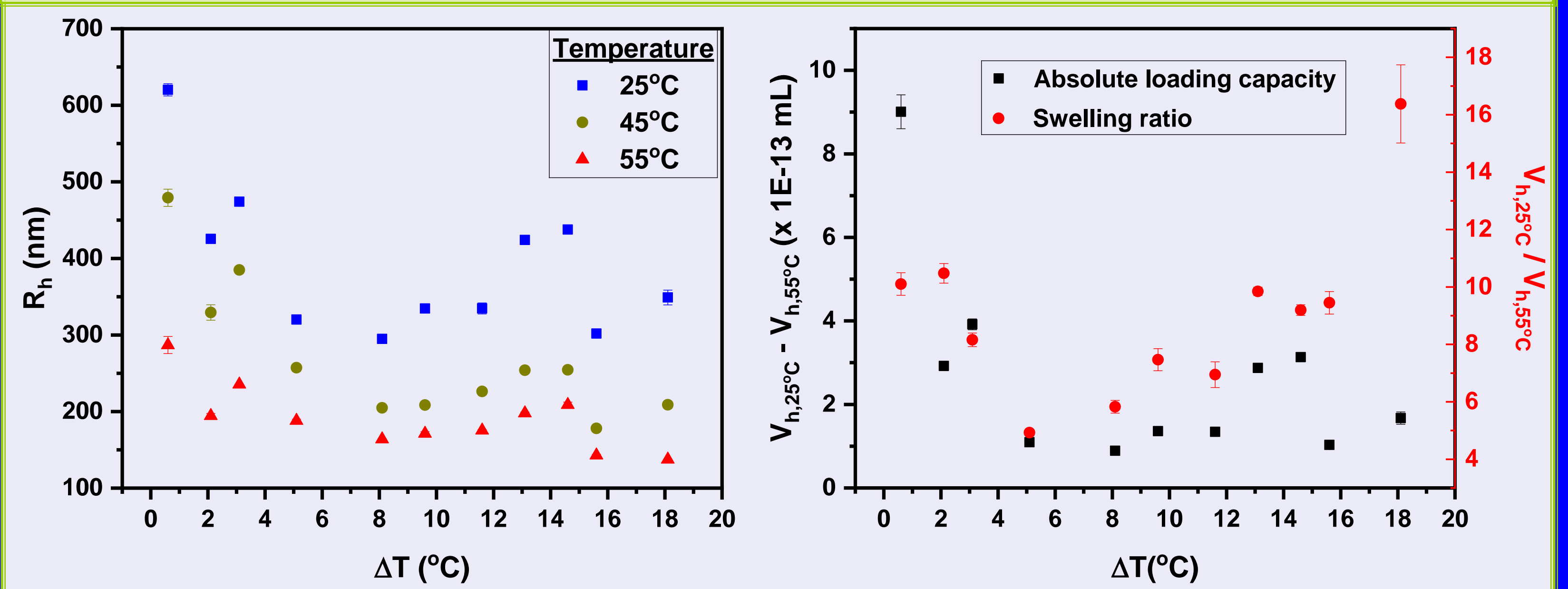
• Dynamic light scattering yielded the hydrodynamic radius, R_h, for each of the samples synthesized at varying synthesis temperatures ($\Delta T = T_{synthesis} - T_C$). We show these results at three solution temperatures above.

• ΔT appears to strongly impact both the swollen size and relative loading capacity of synthesized particles:
  • The smallest particles are obtained with a moderate ΔT, while extreme ΔT values produce larger particles with greater degrees of deswelling.
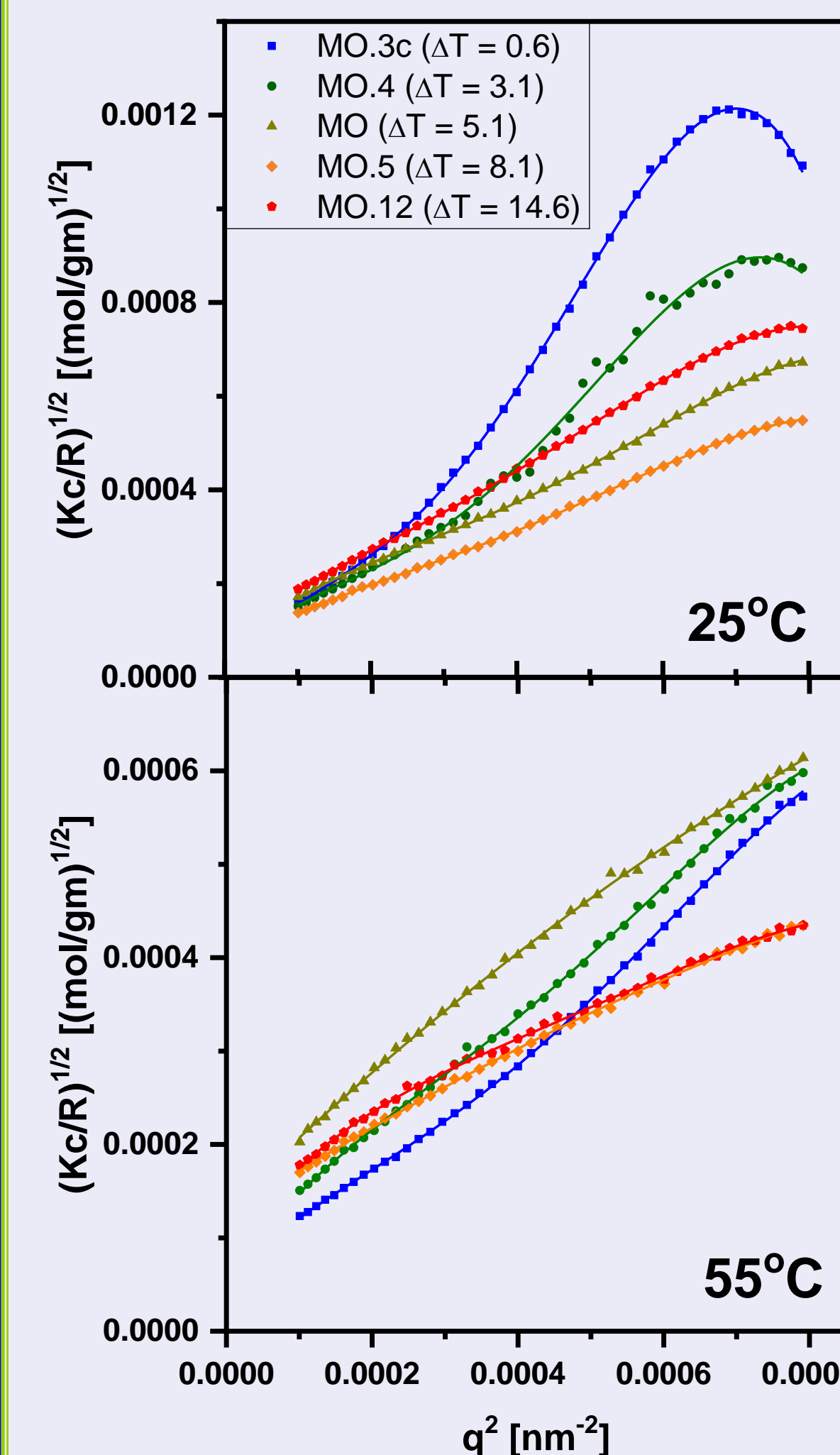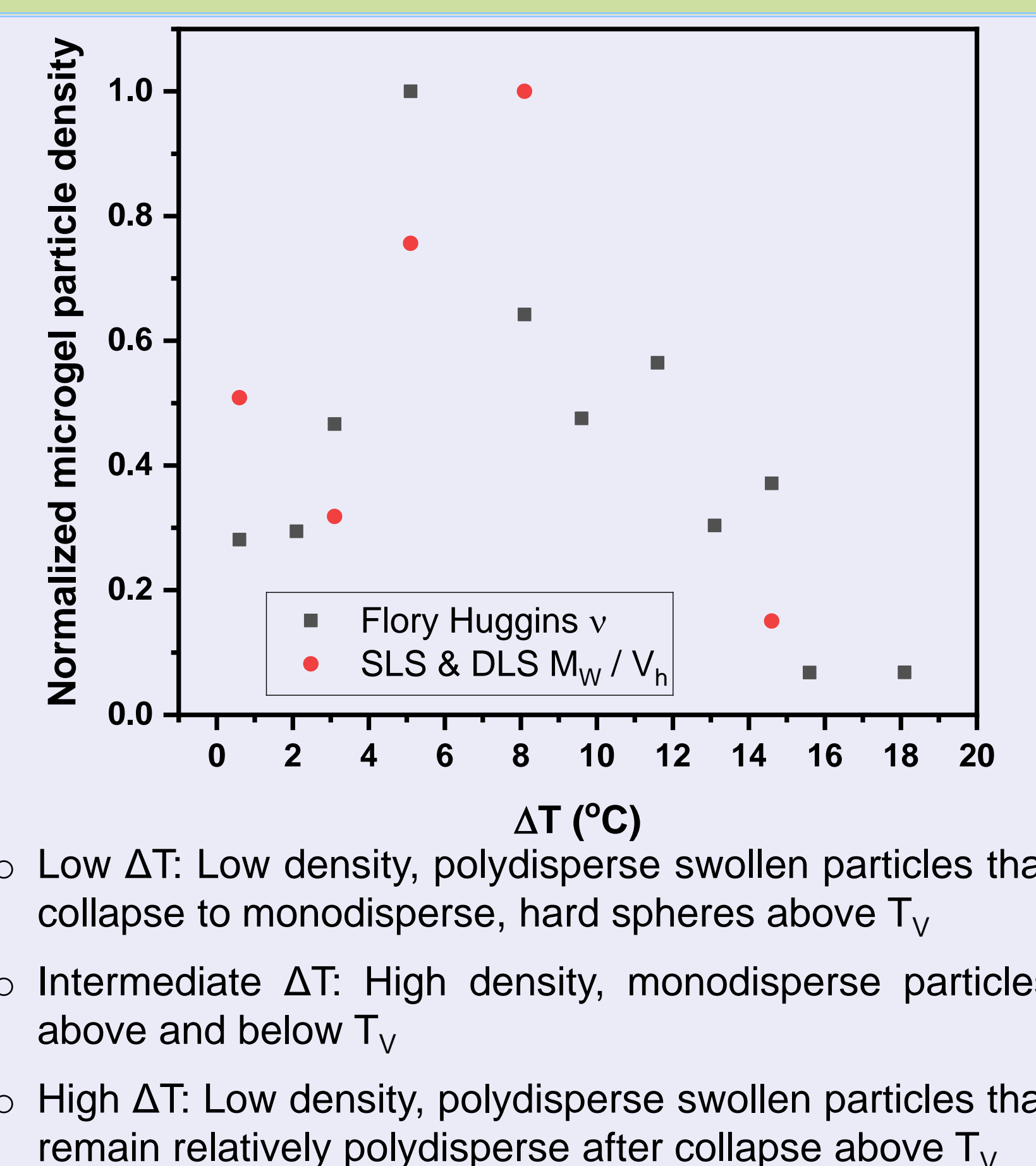
2) Particle polydispersity
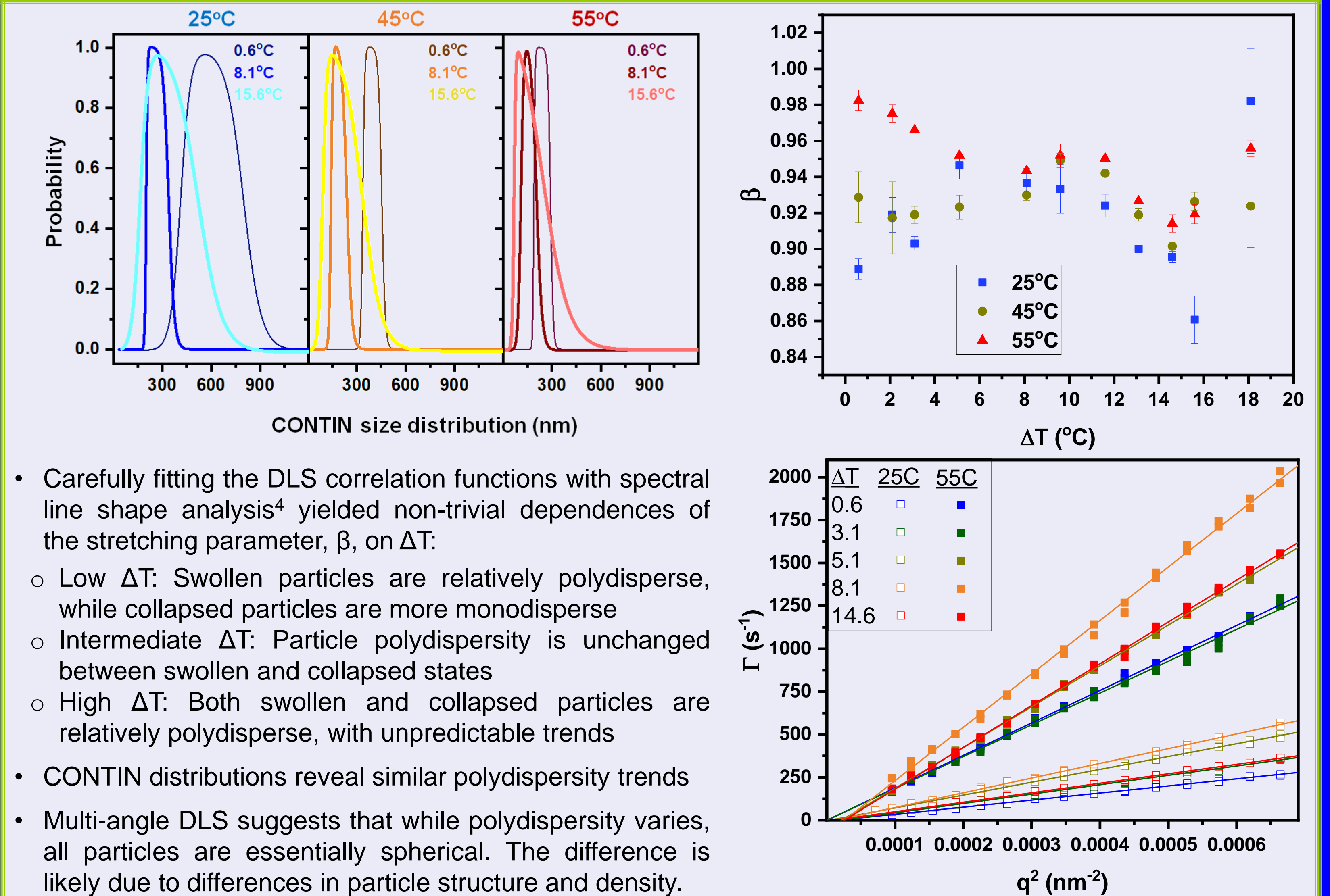
• Carefully fitting the DLS correlation functions with spectral line shape analysis[4] yielded non-trivial dependences of the stretching parameter, β, on ΔT:
  ○ Low ΔT: Swollen particles are relatively polydisperse, while collapsed particles are more monodisperse
  ○ Intermediate ΔT: Particle polydispersity is unchanged between swollen and collapsed states
  ○ High ΔT: Both swollen and collapsed particles are relatively polydisperse, with unpredictable trends

• CONTIN distributions reveal similar polydispersity trends

• Multi-angle DLS suggests that while polydispersity varies, all particles are essentially spherical. The difference is likely due to differences in particle structure and density.

3) Particle density

• We obtained the relative swollen particle densities with two methods:
  • Flory Huggins fits to DLS shrinkage curves yield a theoretical # of chains per particle, ν
  • SLS experiments, when performed at 25°C with unchanged optical settings across a series of samples, yield the relative molecular weights of the swollen particles
  • Dividing the SLS-obtained M_W with the particle volume (obtained by assuming a spherical shape and using the measured R_h values reported above) yields a fully-experimental swollen particle density

Combining SLS and DLS experiments with theory:

○ Low ΔT: Low density, polydisperse swollen particles that collapse to monodisperse, hard spheres above T_V

○ Intermediate ΔT: High density, monodisperse particles above and below T_V

○ High ΔT: Low density, polydisperse swollen particles that remain relatively polydisperse after collapse above T_V

References and Acknowledgements

References:
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4: Phillies, G. D. J.; O'Connell, R.; Whitford, P.; Streletzky, K.A. *J. Chem. Phys.* 119, 9903-9913 (**2003**); Streletzky, K. A.; McKenna, J. T.; Mohieddine, R. J. *Polym. Sci. Part B-Polym. Phys.* **2008**, 46, 771-781.