Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information for: Conformational change and suppression of the Θ-temperature for solutions of polymer-grafted nanoparticles

Katrina Irene S. Mongcopa,[†,‖] Ryan Poling-Skutvik,[‡,‖] Rana Ashkar,[¶,§,⊥] Paul Butler,[¶] and Ramanan Krishnamoorti[*,‡]

† *Materials Science and Engineering, University of Houston, Houston, TX 77204.*
‡ *Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204*

¶ *National Institute of Standards and Technology Center for Neutron Research, Gaithersburg, MD 20899*

§ *Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742*

‖ *Authors contributed equally to this work*
⊥ *Present address: Department of Physics, Virginia Tech, Blacksburg, VA 24061*

E-mail: ramanan@uh.edu

The scattering intensity from polymer-grafted nanoparticles is difficult to model due to the contributions from the various components. Many models have been proposed to extract structural information from the scattering pattern, three of which are compared here to assess their quality in fitting our data. All three models are based on a spherical core with layered structure and include a Lorentzian component to capture the polymer contribution at high-Q. The models differ in how they model the scattering length density (SLD) profile within the shell(s). All fits were performed in the SASView software

For the core-shell model described in Ref. [S1] and in the main body of the text, a single shell exists around the spherical core with a constant SLD value. Both the onion exponential model and the spherical SLD models introduce many additional fitting parameters due to the possibility of more complex SLD profiles present in the shell(s). For the onion exponential model described in Ref. [S2], multiple shells can be included with different exponential SLD profiles. The spherical SLD model also described in Ref. [S2] extends the onion exponential model to have non-exponential SLD profiles. We fit representative data sets for the 67 kDa sample (Fig. S1) using these three models.

For fitting, we use a single shell for all three models and restrict the SLD profiles between $\rho_{\mathrm{PS}} = 1.41 \times 10^{-6}$ Å^{-1} and $\rho_{\mathrm{solv}} = 6.67 \times 10^{-6}$ Å^{-1}. Other constants are the same as those described in the main text. The onion exponential fitting model converges to a flat SLD profile and becomes indistinguishable from the fit using the core-shell model. For the spherical SLD profile, fits using different SLD functional forms are indistinguishable and the fits do not accurately model the data across the full wavevector range due to the inability of the model to handle shell polydispersity. We also note that the inclusion of more fitting parameters within these models makes them very sensitive to the initial estimate and causes them to converge to many different local minima. Although the polymer concentration is expected to have a radial dependence within the grafted corona, the resolution of the SANS data prevents us from distinguishing between different potential profiles within the shell. Thus, we use the simpler core-shell model as a close approximation of the structure of these polymer-grafted nanoparticles in solution.

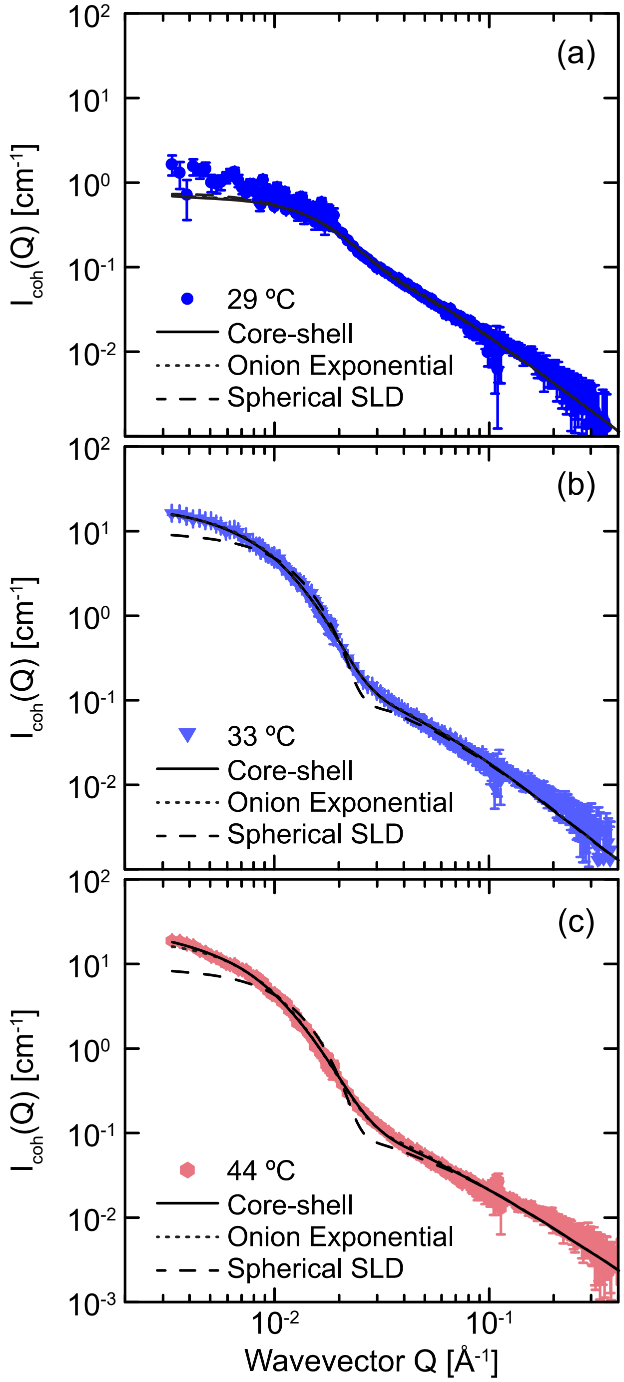

Figure S1: Comparison of different fitting forms to scattering intensities from the 67 kDa sample at different representative temperatures of (a) 29, (b) 33, and (c) 44 °C. Solid curve corresponds to core-shell model described in main text, dotted curve corresponds to onion exponential model, and dashed curve corresponds to spherical SLD model.

References

(S1) Guinier, A.; Fournet, G. *Small-Angle Scattering of X-Rays*; John Wiley and Sons: New York, 1955.

(S2) Feigin, L. A.; Svergun, D. I.; Taylor, G. W. *Struct. Anal. by Small-Angle X-Ray Neutron Scatt.*; Springer US: Boston, MA, 1987; pp 25–55.