Supplemental Information for:

When Does a Macromolecule Transition from a Polymer Chain to a Nanoparticle?

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Structural Characterization of PEHMA NPs using SANS

Previous studies by Martin et al have very well structurally characterized soft polystyrene nanoparticles.[1] The polystyrene nanoparticles were found to maintain a structure of a crosslinked core and corona-esque "fuzzy" outer layer comprised of loops and chain ends. The scattering curves portray two distinctive structures at differing length scales, from the overall nanoparticle's size and shape, and from correlations among the crosslinks within the core. In order to account for these two structures, the scattering curve is fit to a combined model as shown in Equation SI.1.

$$I|q|_{cm^{-1}} = \frac{\phi}{V}(\Delta\rho)^2 \langle P(q)^2 \rangle S(q) + I_{network} + I_{background} \qquad \text{Eq SI.1}$$

Where ϕ is the volume fraction of the nanoparticle, V is the volume of the nanoparticle, $\Delta\rho$ is the contrast between scattering length densities of the nanoparticle and solvent, $\langle P(q)^2 \rangle$ is the average single particle form factor over the particle's size distribution, and $S(q)$ is the inter-particle structure factor, however because the SANS measurements are completed with dilute solutions, there are negligible interactions between objects in the solution and $S(q) = 1$. The form factor, $P(q)$, used describes a spherical particle with a fuzzy interface and is given in Equation SI.2

Eq SI.2

$$P(q) = \frac{3\left[\sin\left(qR_c\right) - qR_c(\cos\left(qR_c\right))\right]}{(qR_c)^3} exp\left(\frac{-(\tau_{fuzzy}q)^2}{2}\right)$$

Here, R_c described the radius of the crosslinked core and τ_{fuzzy} is the half-width of the fuzzy interface. The term of τ_{fuzzy} is defined as the length scale where the scattering length density has decreased to half that of the core's value. The second term, $I_{network}$, captures the influence the crosslinking network within the core has on the particle's scattering, and is described using a Gaussian Lorentz gel model as given in Equation SI.3.

$$I_{network} = I_G(0)exp\left(\frac{-q^2\Xi^2}{2}\right) + \frac{I_L(0)}{1 + q^2\xi^2} \qquad \text{Eq SI.3}$$

Here, $I_G(0)$ and $I_L(0)$ describe the scaling factors of the Gaussian and Lorentzian components respectively, while Ξ and ξ describe the static and dynamic correlations of polymer chains between crosslinks. It was found that the PEHMA nanostructures with a measurable crosslinking density adhered to the same fuzzy sphere-Gauss Lortenz gel combined model previously used for the PS nanoparticles. Each nanostructure with a measurable crosslinking density was fit to the above-described model, minimizing the fitting curve's χ^2 value to confirm optimal fits of the SANS data. Since this combined model accurately describes soft nanostructures of any crosslinking density, signifying two distinct structures at differing length scales, there is no evidence of any non-crosslinked (linear) chains in the scattering sample. Therefore a polymerization is completed using some amount of crosslinker minimal linear (non-crosslinked) chains are expect to exist. The results of this fitting procedure for each nanoparticle are provided in Figures SI.1-6, while the particle core radius, breadth of fuzzy interface, and effective fuzziness of each nanostructure are provided in Table SI.1. All of the fitting was completed within SASView.[2]

χ^a (mol%)	R_c^b(nm)	τ^b (nm)	σ^c	Radius of Gyration (nm)
0%	-	-	-	15.5
0.4%	4.38	7.17	0.38	12.9
0.81%	5.73	5.12	0.32	9.3

The linear (0%XL) PEHMA sample's SANS data does not suggest there are two distinct structures within the polymer and as a result, the combined Fuzzy Sphere-Gauss Lorentz Gel model does not accurately describe the linear chains. Instead, as expected out of a self-avoiding walk linear polymer chain, the 0%XL PEHMA sample is best characterized using the polymer excluded volume model as given in Equation SI.4

$$P(q) = \frac{1}{\nu U^{1/2\nu}} \left\{ \gamma\left(\frac{1}{2\nu},U\right) - \frac{1}{U^{1/2\nu}} \gamma\left(\frac{1}{2\nu},U\right) \right\}$$ Eq SI.4

Where $\gamma(x,U)$ is the incomplete gamma function defined as

$$\gamma(x,U) = \int_0^U dt \, exp\left(-t\right)t^{x-1}$$ Eq SI.5

In Equations SI.4 and SI.5, U is a variable in terms of the scattering vector, q, the radius of gyration of the polymer, R_g, and the excluded volume parameter, ν and is described in Equation SI.6.

$$U = \frac{q^2 R_g^2 (2\nu+1)(2\nu+2)}{6}$$ Eq SI.6

The structural parameters defined by the Fuzzy Sphere model follow a trend with the increasing crosslinking density of the nanostructures. With increasing crosslinking density, the radius of the core of the nanostructure increases, while the breadth of the fuzzy interface decreases. The trend

is true for all of the nanostructures with a measurable crosslinking density, except in the 10.7% XL sample, or the highest crosslinking density nanostructure characterized. This is a result of the molecular weight of the 10.7% XL nanostructure being much lower than its lower crosslinking counterparts. Since $I(0) \sim M_w$ it can be qualitatively observed that the molecular weight of the 10.7% XL nanostructure is close to the same as the 0.4% XL nanostructure and much lower than the other characterized samples. However the effective fuzziness parameter,σ, is a useful tool to compare the fuzziness between samples of differing molecular weights. Using this metric, the trend of decreasing effective fuzziness with increasing crosslinking density holds for all characterized PEHMA samples.

1.   Martin, H. J.; White, B. T.; Scanlon, C. J.; Saito, T.; Dadmun, M. D., Tunable synthetic control of soft polymeric nanoparticle morphology. *Soft Matter* **2017,** *13* (46), 8849-8857.
2.   SasView. http://www.sasview.org/.
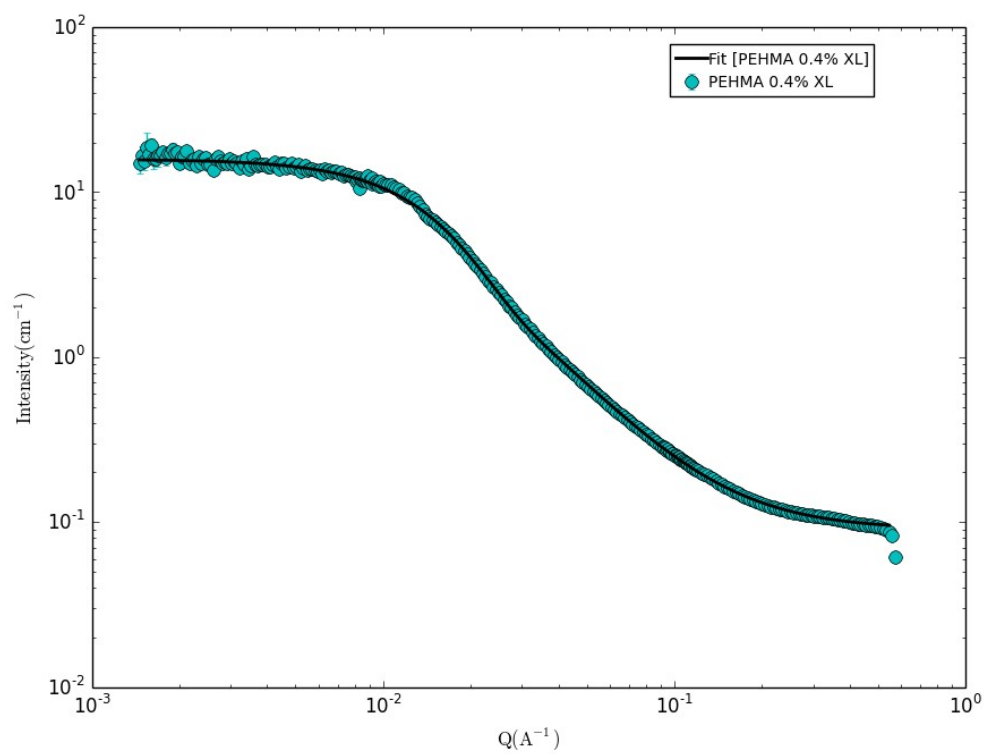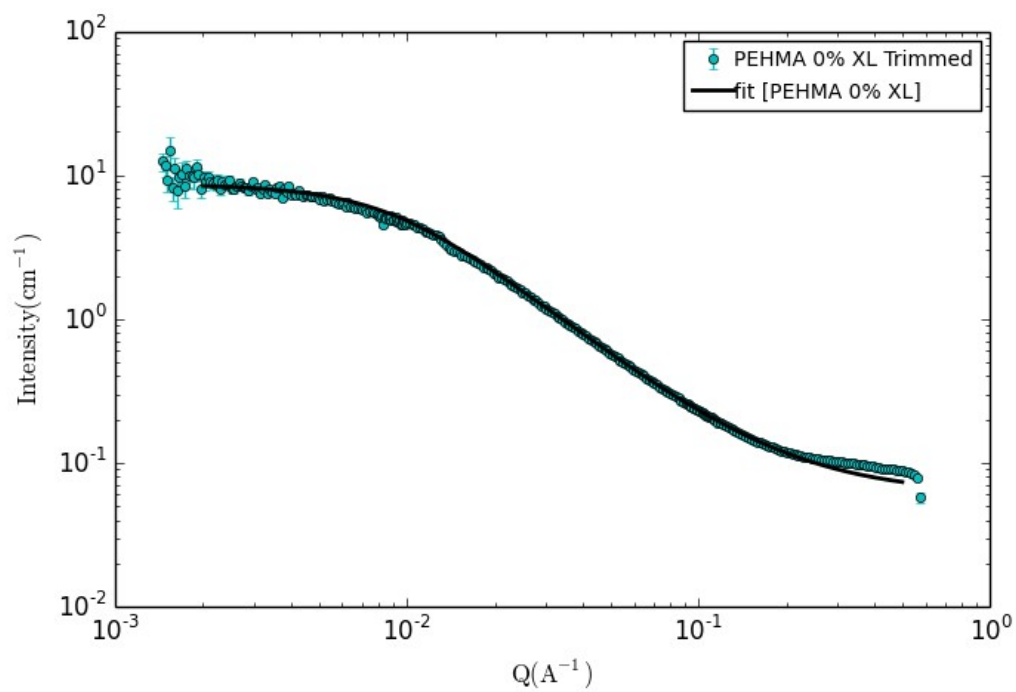
Po Figure SI.2 SANS data of 0.4% XL PEHMA nanostructure in a 1%wt d_8-THF solution fit with the Fuzzy Sphere-Gauss Lorentz Gel combined model
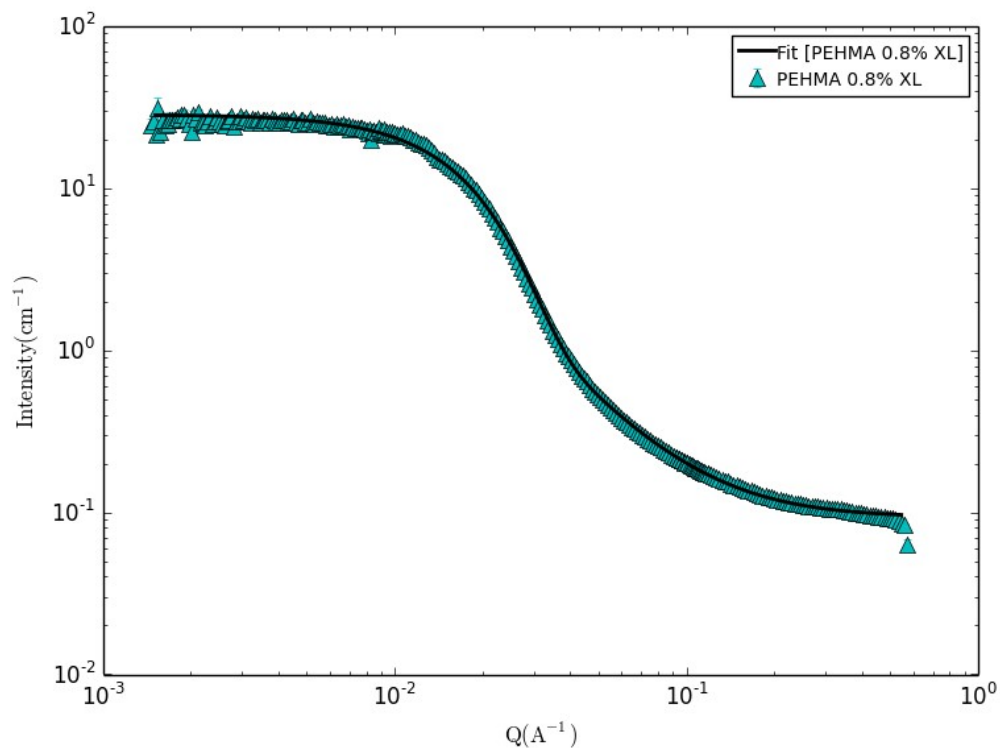
Figure SI.3 SANS data of 0.8% XL PEHMA nanostructure in a 1%wt d_8-THF solution fit with the Fuzzy Sphere-Gauss Lorentz Gel combined model
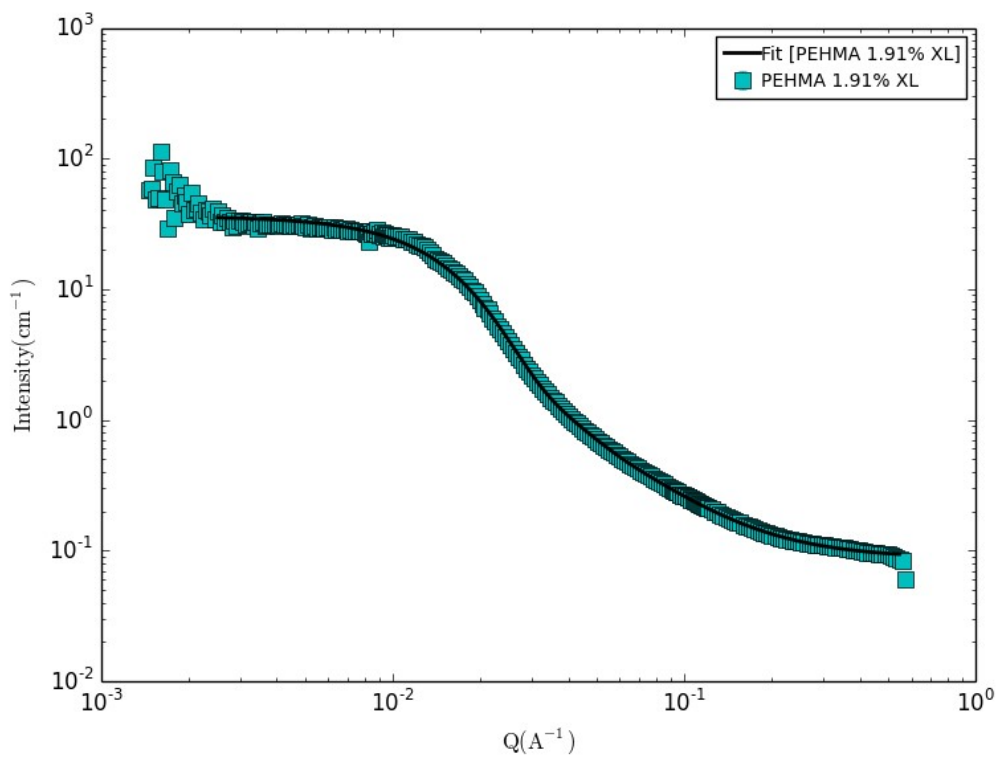

Figure SI.4 SANS data of 1.91% XL PEHMA nanostructure in a 1%wt d_8-THF solution fit with the Fuzzy Sphere-Gauss Lorentz Gel combined model
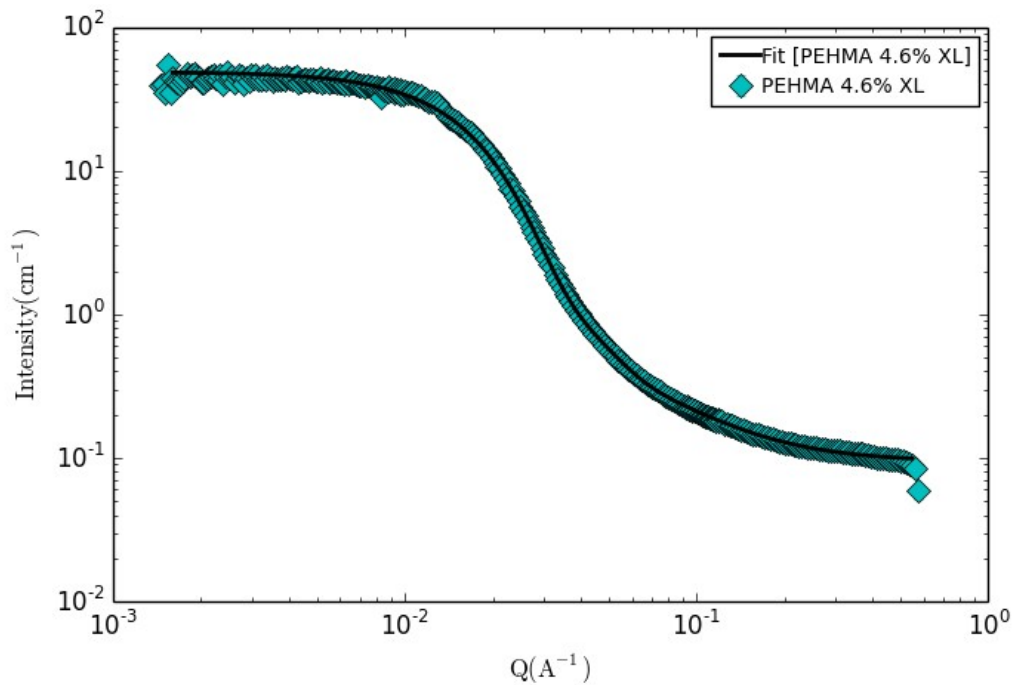
Figure SI.5 SANS data of 4.6% XL PEHMA nanostructure in a 1%wt d_8-THF solution fit with the Fuzzy Sphere-Gauss Lorentz Gel combined model
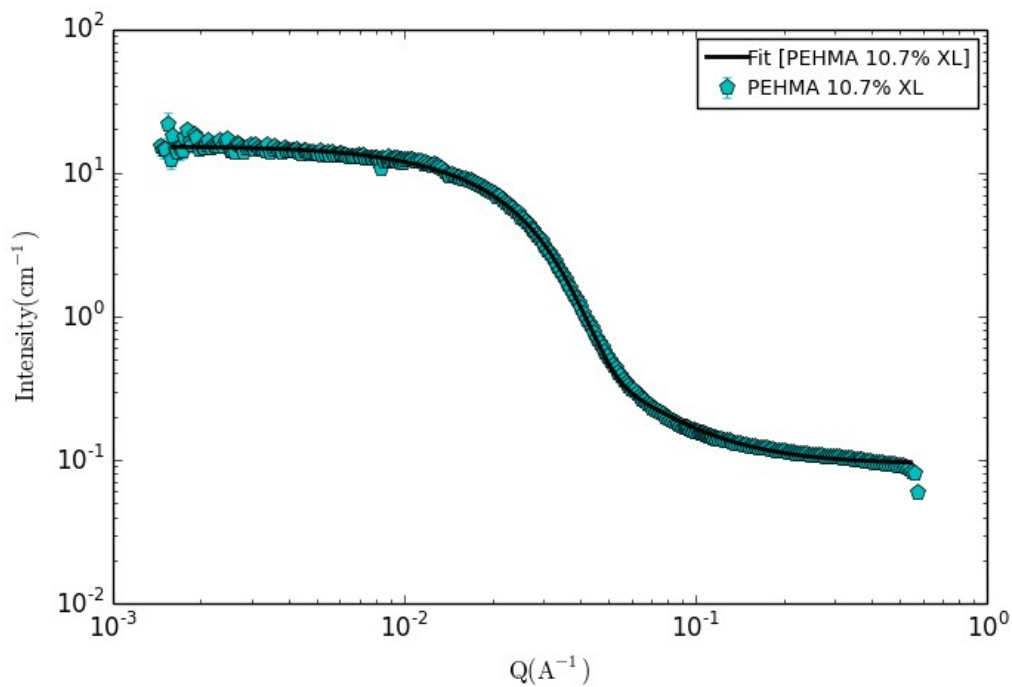

Figure SI.6 SANS data of 10.7% XL PEHMA nanostructure in a 1%wt d_8-THF solution fit with the Fuzzy Sphere-Gauss Lorentz Gel combined model