Appendix D

THE SPHERICAL CORE-SHELL FORM FACTOR APPLIED TO COIL-LIQUID CRYSTALLINE DIBLOCK COPOLYMER MICELLES

D.1 Appendix

A spherical particle having a total radius R_s composed of a core of radius R_c surrounded by a shell of thickness $R_s - R_c$ is assumed to have uniform scattering length density in the core, ρ_c, and in the shell, ρ_s. The surrounding solvent has a scattering length density ρ_{solv}. (Figure D.1). The form factor, $P(q)$, of the particle is given by[1]

$$P(q) = \left[V_c^2(\rho_c - \rho_s)^2\psi_c^2 + 2V_cV_s(\rho_c - \rho_s)(\rho_s - \rho_{solv})\psi_c\psi_s + V_s^2(\rho_s - \rho_{solv})^2\psi_s^2\right] \quad \text{(D.1)}$$

where V_c and V_s are the volumes of the core and shell, respectively, and

$$\psi_x = \frac{3[\sin(qR_x) - qR_x\cos(qR_x)]}{(qR_x)^3}. \quad \text{(D.2)}$$

The first and last terms in Equation D.1 describe the scattering from the core and from the overall particle, respectively. The middle term (cross term) accounts for the interference between the two. The scattered intensity in the absence of interparticle correlations ($S(q) = 1$) is

$$I(q) = KP(q). \quad \text{(D.3)}$$

The proportionality constant K is related to the number of scatterers and is, effectively, simply a fitting parameter.

In the case of a polystyrene (PS) – liquid crystal polymer (LCP) diblock copolymer micelle dissolved in perdeuterated 5CB (d_{19}5CB), PS segregates into the core and the shell contains the LCP block. These cannot be assumed to consist of pure polymer because the penetration of d_{19}5CB into the micelle dilutes the core such that the volume fraction of PS is $f_{PS} < 1$ and the remaining volume is occupied by solvent. Similarly, the volume fraction of LCP in the shell is $f_{LCP} < 1$ and the remaining volume is occupied by solvent. The scattering length density of the core and shell are then calculated from

$$\rho_c = f_{PS}\rho_{PS} + (1 - f_{PS})\rho_{d_{19}5CB} \tag{D.4}$$

$$\rho_s = f_{LCP}\rho_{LCP} + (1 - f_{LCP})\rho_{d_{19}5CB} \tag{D.5}$$

where ρ_{PS} and ρ_{LCP} are the scattering length densities of PS and LCP, respectively, and the scattering length density of the solvent is $\rho_{d_{19}5CB}$. The contrast factors, (ρ_c-ρ_s) and (ρ_s-ρ_{solv}), then become

$$\rho_c - \rho_s = f_{PS}\left(\rho_{PS} - \rho_{d_{19}5CB}\right) - f_{LCP}\left(\rho_{LCP} - \rho_{d_{19}5CB}\right) \tag{D.6}$$

And

$$\rho_c - \rho_{solv} = f_{LCP}\left(\rho_{LCP} - \rho_{d_{19}5CB}\right) \tag{D.7}$$

A relationship between f_{PS} and f_{LCP} is derived from the requirement that the number of LCP chains in the shell must equal the number of PS chains in the core by virtue of the diblock copolymer's connectivity. In other words, the aggregation number of the core must equal that of the shell, expressed mathematically as

$$\frac{f_{PS}\,{}^4\!/_3\,\pi R_c^3}{v_{PS}} = \frac{f_{LCP}\left({}^4\!/_3\,\pi R_s^3 - {}^4\!/_3\,\pi R_c^3\right)}{v_{LCP}} \tag{D.8}$$

where v_{PS} and v_{LCP} are the volumes occupied by a single PS block and LCP block, respectively. Equation D.8 gives the following relationship between f_{PS} and f_{LCP}:

$$f_{LCP} = f_{PS}\frac{v_{LCP}}{v_{PS}}\frac{R_c^3}{R_s^3 - R_c^3}\,. \tag{D.9}$$

Eliminating f_{LCP} from Equations D.6 and D.7 by substituting Equation D.9 gives the contrast factors in terms of f_{PS} alone:

$$\rho_c - \rho_s = f_{PS}\left[\left(\rho_{PS} - \rho_{d_{19}5CB}\right) - \frac{v_{LCP}}{v_{PS}}\frac{R_c^3}{R_s^3 - R_c^3}\left(\rho_{LCP} - \rho_{d_{19}5CB}\right)\right] \tag{D.10}$$

$$\rho_s - \rho_{solv} = f_{PS}\left[\frac{v_{LCP}}{v_{PS}}\frac{R_c^3}{R_s^3 - R_c^3}\left(\rho_{LCP} - \rho_{d_{19}5CB}\right)\right]. \tag{D.11}$$

The form factor for the swollen PS-LCP micelle is now written

$$P(q) = \left[V_c^2 K_c \psi_c^2 + 2V_c V_s K_{cs} \psi_c \psi_s + V_s^2 K_s \psi_s^2\right] \tag{D.12}$$

where

$$K_c = f_{PS}^2\left[\left(\rho_{PS} - \rho_{d_{19}5CB}\right) - \frac{v_{LCP}}{v_{PS}}\frac{R_c^3}{R_s^3 - R_c^3}\left(\rho_{LCP} - \rho_{d_{19}5CB}\right)\right]^2,$$

$$K_{cs} = f_{PS}^2\left[\left(\rho_{PS} - \rho_{d_{19}5CB}\right) - \frac{v_{LCP}}{v_{PS}}\frac{R_c^3}{R_s^3 - R_c^3}\left(\rho_{LCP} - \rho_{d_{19}5CB}\right)\right]\left[\frac{v_{LCP}}{v_{PS}}\frac{R_c^3}{R_s^3 - R_c^3}\left(\rho_{LCP} - \rho_{d_{19}5CB}\right)\right],$$

and

$$K_s = f_{PS}^2\left[\frac{v_{LCP}}{v_{PS}}\frac{R_c^3}{R_s^3 - R_c^3}\left(\rho_{LCP} - \rho_{d_{19}5CB}\right)\right]^2.$$

Evidently, the volume fraction of PS in the core is a multiplicative factor that may be absorbed into the proportionality constant, K, when calculating the scattered intensity (Equation D.3). This implies that the degree to which solvent penetrates the micelle cannot be measured with SANS unless additional information can be gleaned from the interparticle structure factor. The aggregation number is similarly indeterminate from form factor scattering alone, though an upper bound may be established by setting $f_{PS} = 1$.

For the purposes of fitting experimental SANS data the scattered intensity calculated from Equations D.3 and D.12 contains only three adjustable parameters: K, R_c, and R_s. The scattering length densities (ρ_{PS}, ρ_{LCP}, and $\rho_{d_{19}5CB}$) are calculated from the chemical composition of each species using

$$\rho = \frac{\sum_{i=1}^{n} b_{c_i}}{v_m} \tag{D.13}$$

where the b_cs are the bound coherent scattering lengths of the molecule's n atoms and v_m is the molecular volume. Results for the polymers and solvent studied here are summarized in Table D.1.

It is interesting to speculate on the potential use of contrast matching techniques to simplify the scattering from these micelles. If the scattering length density of the shell is equal to that of the solvent, the form factor is reduced to that of a homogeneous sphere,

$$P(q) = V_c^2 (\rho_c - \rho_s)^2 \psi_c^2 , \tag{D.14}$$

and the scattering only depends on one length scale, R_c. However, matching the scattering length density of the solvent and the core does not eliminate any terms from the form factor. Only when $\rho_c = \rho_s$ does the form factor get simpler, reducing to that of a homogenous sphere with radius R_s.

The high incoherent scattering length of hydrogen makes it undesirable to use hydrogenated 5CB as the solvent, but mixtures of 5CB and d_{19}5CB could make suitable solvents if the mixture was less than perhaps 50 % 5CB. Deuterium atoms must be incorporated into the polymer in order to achieve a contrast match with the solvent. Polystyrene is the most obvious candidate for deuteration because styrene monomer containing 1, 2, 3, 5, 6, or 8 deuterons (Table D.2) is readily available from chemical suppliers. However, this is not particularly helpful since contrast matching the core does not eliminate a length scale; even an empty shell is still characterized by R_c and R_s. The complete form factor for a diblock micelle having a contrast-matched core is

$$P(q) = f_{PS}^2 \left[\frac{v_{LCP}}{v_{PS}} \frac{R_c^3}{R_s^3 - R_c^3} \left(\rho_{LCP} - \rho_{d_{19}5CB} \right) \right]^2 \left[V_c^2 \psi_c^2 - 2 V_c V_s \psi_c \psi_s + V_s^2 \psi_s^2 \right]. \tag{D.15}$$

The alternative is to incorporate deuterium into the LCP block, a difficult problem from the synthetic point of view. It may be possible to fully deuterate the mesogens' aromatic rings with techniques similar to those used to synthesize d_{19}5CB and d_2HSiCB4 (Appendix B). Additional deuterons could be incorporated by using a perdeuterated polybutadiene (d_8PB) backbone as the prepolymer. If achievable, these two substitutions would raise the scattering length density of HSiCB4 from 0.9 x 10^{-6} Å^{-2} to 2.8 x 10^{-6} Å^{-2} which would be contrast matched with a mixture of 30 % d_{19}5CB / 70% 5CB (ρ_{5CB} = 1.4 x 10^{-6} Å^{-2}), a mixture that is likely too high in hydrogen content. In order to achieve a contrast match between HSiCB4 and a 50/50 mixture of d_{19}5CB/5CB, 22 of the polymer's 35 hydrogens must be replaced with deuterium atoms (Figure D.2). This would require deuterium substitution of all hydrogens except those on the siloxane linking group.

Notably from Figure D.2, the scattering length density of d_2HSiCB4 is almost perfectly matched to that of PS. This match does not, however, imply that a d_2HSiCB4-PS diblock would form a micelle with matched core and shell. Note that all of the contrast terms in Equation D.12 are relative to the solvent; none are between the two polymers. The solvent penetrates the core and shell to different degrees such that $\rho_c \neq \rho_s$, even when $\rho_{LCP} = \rho_{PS}$.

D.2 Tables

Table D.1 Densities and scattering length densities, ρ, of relevant molecules.

	Density [g/cm^3]	$\rho \times 10^6$ [Å^{-2}]
d_{19}5CB	1.1[a]	6.2
HSiCB4	1.0[a]	0.9
HSiBB	1.0[a]	1.0
PS	1.05	1.4
PB	0.9	0.4

[a] Estimated density; actual value unknown

Table D.2 Densities and scattering length densities, ρ, of polystyrene having various levels of deuteration.

Number of Deuterons	Density [g/cm^3]	$\rho \times 10^6$ [Å^{-2}]
0	1.05	1.4
1	1.06[a]	2.0
2	1.07[a]	2.6
3	1.08[a]	3.2
5	1.10[a]	4.4
6	1.11[a]	4.9
8	1.13[a]	6.5

[a] Estimated density; actual value unknown

D.3 Figures

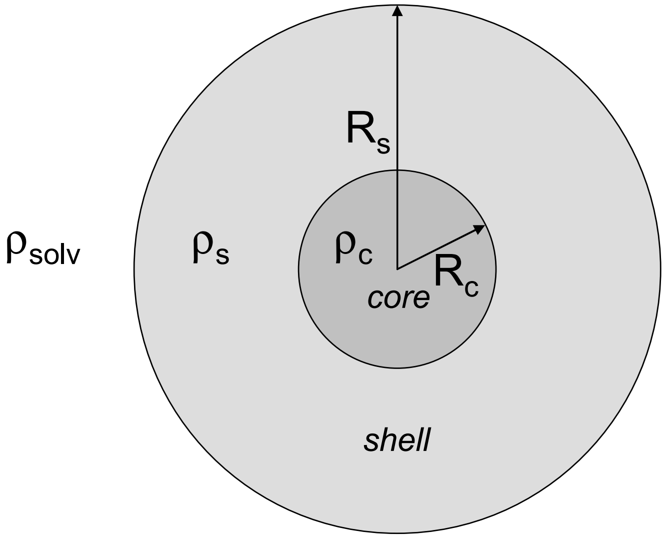

Figure D.1 Schematic diagram of a spherical core-shell particle having an overall radius R_s and a core radius of R_c. The scattering length densities of the core and corona (ρ_c and ρ_s, respectively) are assumed be uniform throughout their respective volumes. The particle is in a solvent with scattering length density ρ_{solv}.

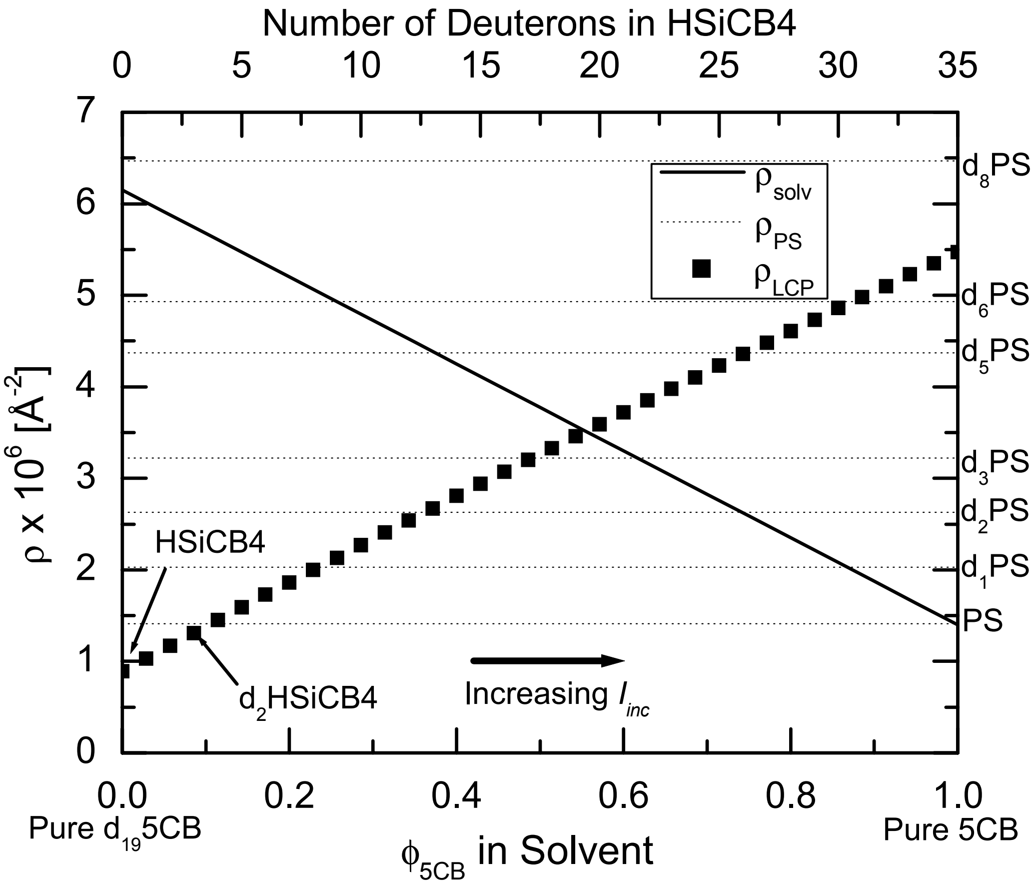

Figure D.2 Achievable neutron scattering length densities of the solvent, side-group liquid crystal polymer (HSiCB4), and polystyrene (PS) by various strategies for changing each component's deuterium content. The deuterium content of the solvent can be varied by mixing d$_{19}$5CB with 5CB (bottom axis) to achieve ρ x 10^6 anywhere between 1.4 and 6.2 Å^{-2} (solid line). As the 5CB content increases, the incoherent scattering (I_{inc}) increases. Deuterium can be incorporated into polystyrene by polymerizing d$_x$-styrene where x is the number of deuterium atoms in the monomer (dotted lines). It might be possible to substitute deuterium for some of the 35 hydrogen atoms on the HSiCB4 monomer (squares, top axis). Only one such deuteriated polymer, d$_2$HSiCB4, has been synthesized to date.

D.4 References

[1] King, S. M.; Griffiths, P. C.; Cosgrove, T. Using SANS to Study Adsorbed Layers in Colloidal Dispersions. In *Applications of Neutron Scattering to Soft Condensed Matter*; B.J. Gabrys, Editor; Gordon and Breach Science Publishers: Amsterdam, 2000.