Electronic Supplementary Information—Influence of an ionic comonomer on polymerization-induced self-assembly of diblock copolymers in non-polar media

Gregory N. Smith,*,[†,‡] Sarah L. Canning,[†,¶] Matthew J. Derry,[†,§] Oleksandr O. Mykhaylyk,[†] Sarah E. Norman,[∥,⊥] and Steven P. Armes*,[†]

†Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, South Yorkshire, S3 7HF, United Kingdom

‡Niels Bohr Institute, University of Copenhagen, H. C. Ørsted Institute, Universitetsparken 5, 2100 Copenhagen Ø, Denmark

¶Current address: Fujifilm Speciality Ink Systems Ltd, Pysons Road, Broadstairs, Kent CT10 2LE, United Kingdom

§Current address: Aston Institute of Materials Research, Aston University, Aston Triangle, Birmingham, B4 7ET, United Kingdom.

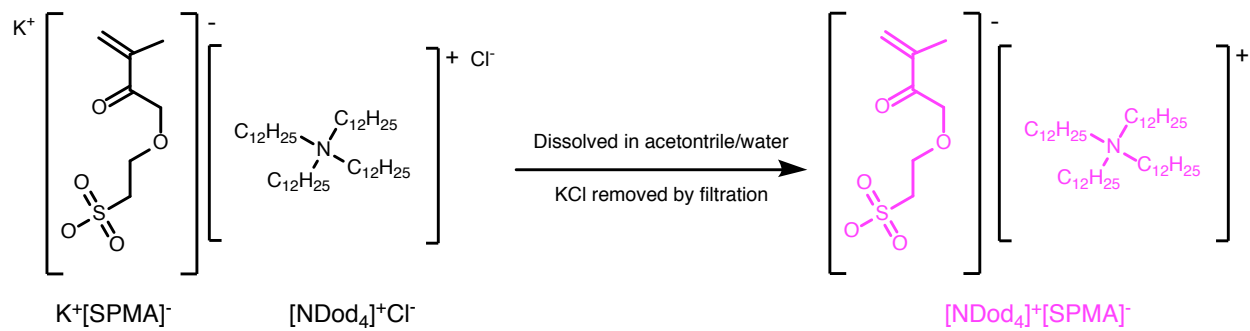∥School of Chemistry and Chemical Engineering, The QUILL Centre, Queen's University Belfast, Belfast BT9 5AG, United Kingdom

⊥Current address: ISIS-STFC, Rutherford Appleton Laboratory, Chilton, Oxon, OX11 0QX, United Kingdom

E-mail: gregory.smith@nbi.ku.dk; s.p.armes@sheffield.ac.uk

1

Materials

Anionic comonomer

Scheme S1: The ion exchange reaction to synthesize the ionic comonomer used in this study, tetradodecylammonium 3-sulfopropyl methacrylate ($[NDod_4]^+[SPMA]^-$).

Methods

Small-angle X-ray scattering

In general, the scattering intensity $(I(Q))$ or equivalently the differential cross section per unit volume $(\mathrm{d}\Sigma/\mathrm{d}\Omega)$ for an object with no distribution in its size is a function of the volume fraction of particles (ϕ), the particle volume (V_p), a contrast term $(\Delta\rho^2)$, the form factor $(P(Q))$ arising from the particle geometry, and the structure factor $(S(Q))$ due to interparticle interactions. Since dilute dispersions were studied, $S(Q)$ can be set equal to 1.

$$\frac{\mathrm{d}\Sigma}{\Omega} \equiv I(Q) = \phi V_p \Delta\rho^2 P(Q)S(Q) \tag{S1}$$

Q is the modulus of the momentum transfer vector and is a function of the scattering angle (2θ) and the wavelength of the radiation (λ).

$$Q = \frac{4\pi \sin\theta}{\lambda} \tag{S2}$$

Equation S1 is only strictly appropriate for homogenous particles, where the shape dependent structural terms $(P(Q)S(Q))$ can be multiplied by a scale factor $(\phi V_p \Delta\rho^2)$. This is not the case for the copolymer micelles, which have a heterogenous composition. Therefore, the form factors will now include terms relating to these prefactors.

The general form factor (P_m) of a diblock copolymer micelle of arbitrary morphology consists of four terms: two self-terms (for the core, P_i, and the chains on the surface, P_s) and two cross-terms (between the core and the chains, S_{ic}, and between different chains on the surface, S_{cc}).[1] The subscript i refers to the form factor used for the core (s for spherical micelles, w for worm-like micelles, and v for vesicular micelles).

$$P_m(Q) = N_i^2 \beta_i^2 P_i(Q) + N_i \beta_c^2 P_c(Q) + 2N_i^2 \beta_i \beta_c S_{ic}(Q) + N_i(N_i - 1)\beta_c^2 S_{cc}(Q) \tag{S3}$$

3

In this expression, N_i is the aggregation number, and β_s and β_c are the total excess scattering lengths of blocks in the core and the shell (chains), respectively. (The scale factor in Equation S1 is modified by the inclusion of the β term.) These are given by $\beta_i = V_i(\rho_i - \rho_m)$ and $\beta_c = V_c(\rho_c - \rho_m)$, where V is the volume of a block and ρ is the scattering length density of a block. ρ_m is the scattering length density of the solvent medium. The form factors for the three morphologies studied in this paper are discussed below.

Spherical micelles ($i = s$)

The scattering model for spherical diblock copolymer micelles has previously been reported.[1,2]

The form factor for the sphere self-term ($P_s(Q)$) is simply the well-known spherical form factor for a sphere of radius r.[3,4]

$$P_s(Q) = \left[\frac{3\left[\sin\left(Qr\right) - Qr\cos\left(Qr\right)\right]}{(Qr)^3} \right]^2 \tag{S4}$$

The self-term for the chains in the corona ($P_c(Q)$) is given by the Debye function, assuming that they are Gaussian chains with a radius of gyration R_g.[5]

$$P_c(Q) = \frac{2\left[\exp\left(-Q^2 R_g^2\right) - 1 + Q^2 R_g^2\right]}{Q^4 R_g^4} \tag{S5}$$

To mimic non-penetration of the Gaussian chains, they are set as starting a distance dR_g away from the surface of the core, where $d \approx 1$. The cross-term between core and chains ($S_{sc}(Q)$) is given by the following expression.

$$S_{sc}(Q) = \Phi(Qr)\psi(QR_g)\frac{\sin\left(Q\left[r + dR_g\right]\right)}{Q\left[r + dR_g\right]} \tag{S6}$$

The functions $\Phi(x)$ and $\psi(x)$ are given below.

$$\Phi(x) = \frac{3\left[\sin\left(x\right) - x\cos\left(x\right)\right]}{(x)^3} \tag{S7}$$

$$\psi(x) = \frac{[1 - \exp(-x)]}{x} \tag{S8}$$

The interference term between chains in the corona ($S_{cc}(Q)$) is given by the following expression.

$$S_{cc}(Q) = \psi^2(QR_g) \left[\frac{\sin(Q[r + dR_g])}{Q[r + dR_g]} \right]^2 \tag{S9}$$

Two modifications have been incorporated into this standard model for spherical diblock copolymer micelles. First, a sigmoidal interface was assumed to account for a varying scattering length density at the micellar interface. The interface width σ was set to 2.5. This modified the interface by the term $\exp(-Q^2\sigma^2/2)$. Next, a radial profile was used to define scattering in the micelle corona using a linear combination of two cubic splines with fitting parameters corresponding to the width and weight coefficient. Further information on these modifications can be found elsewhere. [6–8]

The core radius of the micelles was fit with a Gaussian distribution with standard deviation σ_G, given in the expression below.

$$f_G(x) = \frac{1}{\sqrt{2\pi\sigma_G^2}} \exp\left(-\frac{(x - r)^2}{2\sigma_G^2}\right) \tag{S10}$$

Worm-like micelles ($i = w$)

The scattering model for worm-like diblock copolymer micelles has previously been reported. [2]

The form factor for the worm self-term ($P_w(Q)$) is a product of a core cross-section term (P_{cross}) and a term for the semi-flexible cylinder (P_L).

$$P_w(Q) = P_{cross}(Q, r) P_L(Q, L_w, b_w) \tag{S11}$$

In this expression, r is the cylinder radius, L_w is the mean worm contour length, and b_w is the worm Kuhn length. The core cross-section term is defined below, and $J_1(x)$ is the

first-order Bessel function.

$$P_{cross}(Q, r) = A_{cross}^2(Q, r) = \left[2\frac{J_1(Qr)}{Qr}\right]^2 \tag{S12}$$

P_L describes the scattering from a self-avoiding semi-flexible chain, and a complete expression for the chain form factor can be found elsewhere.[9]

As in the sphere case, the self-term for the chains in the corona $(P_c(Q))$ is given by the Debye function (Equation S5).

The cross-term between worm cores and corona chains (S_{wc}) is given by the following expression, where $\psi(x)$ was defined in Equation S8.

$$S_{wc} = \psi(QR_g)A_{cross}J_0(Q \cdot (r + R_g))F(q, L_w, b_w) \tag{S13}$$

The interference term between chains in the corona (S_{cc}) is given by the following expression.

$$S_{cc}(Q) = \psi^2(QR_g)J_0^2(Q \cdot (r + R_g))F(q, L_w, b_w) \tag{S14}$$

As with the spherical micelles, the core radius of the worm-like micelles was fit with a Gaussian distribution, given in Equation S10.

Vesicular micelles $(i = v)$

The scattering model for vesicular diblock copolymers micelle has previously been reported.[10,11]

The form factor for the vesicle self-term $(P_v(Q))$ is given by the square of the form factor amplitude $(F_v(Q)^2 = P_v(Q))$. The function depends on the inner radius of the membrane (r_{in}) and the outer radius of the membrane (r_{out}), with corresponding spherical volumes V_{in} and V_{out}. The two radii are defined by the membrane radius (r_m), the distance from the center of the vesicle to the midpoint of the membrane, and the thickness of the membrane

(t_m).

$$r_{in} = r_m - \frac{t_m}{2} \tag{S15}$$

$$r_{out} = r_m + \frac{t_m}{2} \tag{S16}$$

There is also a decaying sigmoidal interface term (σ_{in}), which was set to 2.5. The form factor amplitude for the vesicle self-term is given below.

$$F_v(Q) = \frac{V_{out}\Phi(Qr_{out}) - V_{in}\Phi(Qr_{in}}{V_{out} - V_{in}} \cdot \exp\left(-\frac{Q^2\sigma_{in}^2}{2}\right) \tag{S17}$$

The vesicle corona self-term $(P_c(Q))$ is defined as the square of the amplitude of the form factor $(F_c(Q)^2 = P_c(Q))$ is given in the equation below.

$$F_c(Q) = \frac{\psi(QR_g)}{2}\left[\frac{\sin\left(Q \cdot (r_{out} + R_g)\right)}{Q(r_{out} + R_g)} + \frac{\sin\left(Q \cdot (r_{in} - R_g)\right)}{Q(r_{in} - R_g)}\right] \tag{S18}$$

The two cross-terms, the core-corona term (S_{vc}) and the corona chain interference term (S_{cc}) are defined by the form factor amplitudes.

$$S_{vc}(Q) = F_v(Q)F_c(Q) \tag{S19}$$

$$S_{cc}(Q) = F_c^2(Q) \tag{S20}$$

The vesicles are also fit with two size distributions, one for the membrane radius of the vesicles (r_m) and another for the membrane thickness (t_m). Each of the size distributions are given by a Gaussian function (Equation S10).

Material properties

There are three primary non-geometric parameters that need to be introduced into the diblock copolymer micelle scattering models (Equation S3): the volumes of the blocks, the scattering length density (ρ, SLD) of all species, and the stabilizer R_g. The mass densities for PSMA ($\rho_m = 0.904$ g mol^{-1}), PBzMA ($\rho_m = 1.179$ g mol^{-1}), and n-dodecane ($\rho_m = 0.7495$ g mol^{-1}) have been taken from the literature.[12–14] The mass density for the [SPMA]$^-$[NDod]$^+$ monomer is not available, and the molecular volume was calculated using volume increments.[15] Ion dissociation is very low in nonpolar solvents, and so volumes are calculated assuming complete ion binding.

Table S1: Mass densities and molecular volumes of species

	Mass density / (g cm^{-3})	Molecular volume / Å^3
PSMA	0.904	622
PBzMA	1.179	248
PSPMA$^-$	—	178
[NDod$_4$]$^+$	—	843
n-Dodecane	0.7495	170.

To calculate the scattering length densities, both the coherent scattering length (b_i) and the molecular volumes (V_m) must be known.

$$\rho = \frac{\sum_i b_i}{V_m} \tag{S21}$$

For X-rays, as scattering arises from the interaction between X-rays and the atomic electron cloud, b_i is related to the atomic number (Z). At X-ray energies away from absorption edges, the atomic scattering factor f_1 is well approximated by the Z. In this case, b_i is equal to the product of the atomic number and the classical electron radius (r_e).[16,17] For n-dodecane, the PSMA stabilizer, and non-ionic PBzMA, the SLD of a polymer repeat unit is equal to the SLD of the entire polymer. For ionic monomer containing cores, the SLD of the whole

polymer molecule must be calculated, as it is a binary species. Additionally, the SLD of the ionic PSMA is calculated assuming complete ion binding, as the dissociation constant for ions in non-polar solvents is extremely low.

Table S2: X-ray scattering length density of repeat units and materials

	SLD, ρ / (10^{-6} Å^{-2})
PSMA	8.61
PBzMA	10.7
PSPMA$^-$	17.4
[NDod$_4$]$^+$	13.2
n-Dodecane	7.32

All models used for fitting these copolymer micelles assume that the stabilizer is a Gaussian coil with a set radius of gyration (R_g), calculated using Equation S22. L is the contour length, b is the Kuhn length, and $L/b \equiv N$ is the number of Kuhn segments.[18]

$$R_g = \sqrt{\frac{L/b}{6}} \cdot b \equiv \sqrt{\frac{N}{6}} \cdot b \tag{S22}$$

The contour length of the polymers (L) can be calculated as the product of the DP and the projected contour length of each SMA unit (two carbon-carbon bonds in an all-*trans* configuration, 2.55 Å). The Kuhn length (b) of PSMA is 35 Å.[19] From this, the R_g of PSMA$_{18}$ stabilizer is found to be 16.4 Å. For poly(alkyl methacrylates) such as PSMA in an n-alkane, the alkyl (stearyl) sidechains have the same electron density as the solvent. It is, therefore, challenging to model the scattering from the polymer with precision, and the fit values should be interpreted accordingly.

Fitting parameters

SAXS data were fitted using models as described previously. The best fit values are given in the following tables. For all objects, the SLDs are fixed to those calculated from the molecular structure (Table S2), and the volume of the two blocks is fixed that calculated $(V_i = \mathrm{DP} \cdot V_m)$. The geometric parameters are allowed to vary. For all nano-objects studied, the data could be well fitted without including any solvation of the core, and so the term x_{sol} was fixed at 0.

Spheres

For spherical copolymer micelles, the fit parameters of interest are the mean core radius (r), the standard deviation of the Gaussian distribution of the radius (σ_G) with corresponding coefficient of variation ($c_v = \sigma_G/r$), and the stabilizer radius of gyration (R_g). The curves are multiplied by a fit arbitrary scale factor and added to a constant background to give best agreement with the experimental data over the whole Q-range.

Table S3: Spherical micelle fitting parameters

	r / Å	σ_G / Å	$c_v(\sigma_G/r)$	Stabilizer R_g / Å
$[S_{18}–P(Bz_{46}\text{-}stat\text{-}SPMA_1)]^{-1}$	78	8	0.10	11

$[NDod_4]^+$ counterions are excluded for brevity.

Worms

For worm-like copolymer micelles, the fit parameters of interest are the mean worm radius (r), the standard deviation of the Gaussian distribution of the radius (σ_G) with corresponding coefficient of variation ($c_v = \sigma_G/r$), the stabilizer radius of gyration (R_g), the worm contour length (L_w), and the worm Kuhn length (b_w). The curves are multiplied by a fit arbitrary scale factor and added to a constant background to give best agreement with the experimental data over the whole Q-range.

Table S4: Worm-like micelle fitting parameters

	r / Å	σ_G / Å	c_v	R_g / Å	L_w / Å	b_w / Å
$[\text{S}_{18}\text{–P}(\text{Bz}_{102}\text{-}stat\text{-SPMA}_2)]^{-2}$	104	14	0.14	5	9950.	2592

$[\text{NDod}_4]^+$ counterions are excluded for brevity.

Vesicles

For vesicular copolymer micelles, the fit parameters of interest are the mean vesicle membrane radius (r_m), the standard deviation of the Gaussian distribution of the radius ($\sigma_{G,r}$) with corresponding coefficient of variation ($c_{v,r} = \sigma_G/r$), the stabilizer radius of gyration (R_g), the membrane thickness (t_m), and the standard deviation of the Gaussian distribution of the thickness ($\sigma_{G,t}$) with corresponding coefficient of variation ($c_{v,t}$). The curves are multiplied by a fit arbitrary scale factor and added to a constant background to give best agreement with the experimental data over the whole Q-range.

Table S5: Vesicular micelle fitting parameters

	r_m / Å	$\sigma_{G,r}$ / Å	$c_{v,r}$	R_g / Å	t_m / Å	$\sigma_{G,t}$ / Å	$c_{v,t}$
[S$_{18}$–P(Bz$_{309}$-$stat$-SPMA$_9$)]$^{-9}$	833	164	0.20	1	330.	59	0.18

DLS size distributions

To compare Z-average diameters from DLS data require that the size distributions are monomodal and that the particles are nearly spherical. The nonionic $PSMA_{18}$–$PBzMA_y$ and $PSMA_{34}$–$PBzMA_y$ nano-objects synthesized at 20 wt. %, 30 wt. %, and 40 wt. % meet these requirements as shown in Figures S1 and S2.
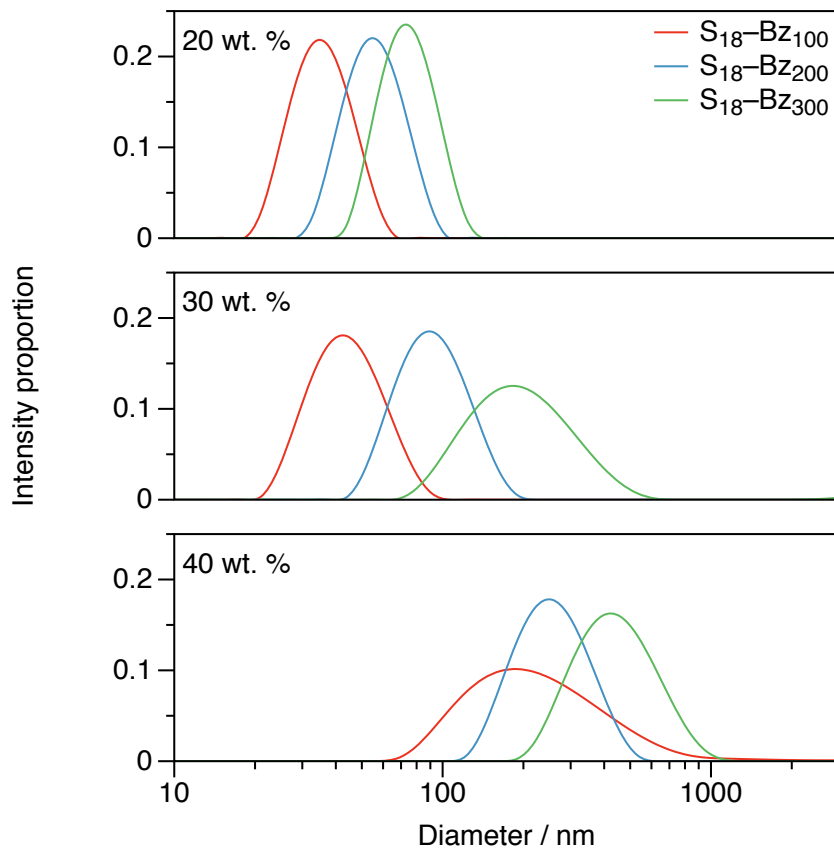

Figure S1: Intensity-weighted particle size distributions from DLS data for $PSMA_{18}$–$PBzMA_y$ nano-objects synthesized in n-dodecane with DPs (y) specified in the legends and synthesized at concentrations (in wt. %) specified in each sub-figure.
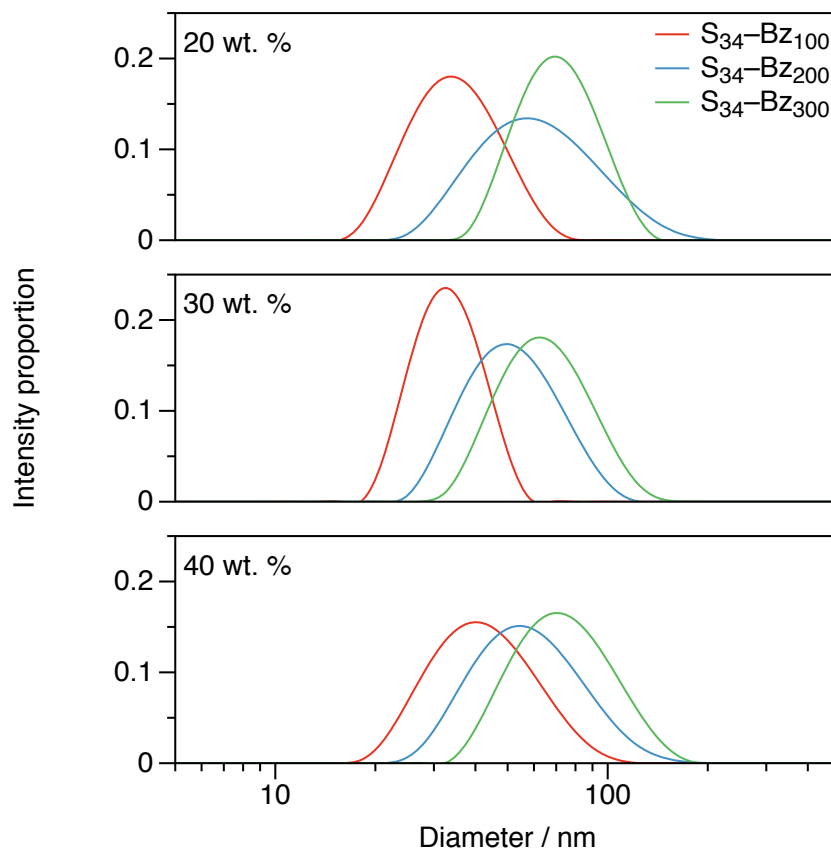
Figure S2: Intensity-weighted particle size distributions from DLS data for $PSMA_{34}$–$PBzMA_y$ nano-objects synthesized in n-dodecane with DPs (y) specified in the legends and synthesized at concentrations (in wt. %) specified in each sub-figure.

References

(1) Pedersen, J. S.; Gerstenberg, M. C. Scattering Form Factor of Block Copolymer Micelles. *Macromolecules* **1996**, *29*, 1363–1365.

(2) Pedersen, J. S. Form factors of block copolymer micelles with spherical, ellipsoidal and cylindrical cores. *J. Appl. Cryst.* **2000**, *33*, 637–640.

(3) Lord Rayleigh, The Incidence of Light upon a Transparent Sphere of Dimensions Comparable with the Wave-Length. *Proc. R. Soc. London A* **1910**, *84*, 25–46.

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

(5) Debye, P. Molecular-weight Determination by Light Scattering. *J. Phys. Chem.* **1947**, *51*, 18–32.

(6) Pedersen, J. S.; Svaneborg, C.; Almdal, K.; Hamley, I. W.; Young, R. N. A Small-Angle Neutron and X-ray Contrast Variation Scattering Study of the Structure of Block Copolymer Micelles: Corona Shape and Excluded Volume Interactions. *Macromolecules* **2003**, *36*, 416–433.

(7) Pedersen, J. S.; Gerstenberg, M. C. The structure of P85 Pluronic block copolymer micelles determined by small-angle neutron scattering. *Colloids Surf. A: Physicochem. Eng. Aspects* **2003**, *213*, 175–187.

(8) Derry, M. J.; Fielding, L. A.; Warren, N. J.; Mable, C. J.; Smith, A. J.; Mykhaylyk, O. O.; Armes, S. P. *In situ* small-angle X-ray scattering studies of sterically-stabilized diblock copolymer nanoparticles formed during polymerization-induced self-assembly in non-polar media. *Chem. Sci.* **2016**, *7*, 5078–5090.

(9) Pedersen, J. S.; Schurtenberger, P. Scattering Functions of Semiflexible Polymers with and without Excluded Volume Effects. *Macromolecules* **1996**, *29*, 7602–7612.

(10) Bang, J.; Jain, S.; Li, Z.; Lodge, T. P.; Pedersen, J. S.; Kesselman, E.; Talmon, Y. Sphere, Cylinder, and Vesicle Nanoaggregates in Poly(styrene-*b*-isoprene) Diblock Copolymer Solutions. *Macromolecules* **2006**, *39*, 1199–1208.

(11) Bang, J.; Jain, S.; Li, Z.; Lodge, T. P.; Pedersen, J. S.; Kesselman, E.; Talmon, Y. Sphere, Cylinder, and Vesicle Nanoaggregates in Poly(styrene-*b*-isoprene) Diblock Copolymer Solutions. Volume 39, Number 3, February 7, 2006, pp 1199–1208. *Macromolecules* **2006**, *39*, 5583.

(12) Rogers, S.; Mandelkern, L. Glass Formation in Polymers. I. The Glass Transitions of the Poly-(*n*-Alkyl Methacrylates). *J. Phys. Chem.* **1957**, *61*, 985–991.

(13) Sigma–Aldrich. http://www.sigmaaldrich.com/united-kingdom.html.

(14) CRC, *CRC Handbook of Chemistry and Physics*, 95th ed.; CRC Press, 2014–2015 (Internet Version).

(15) Edward, J. T. Molecular volumes and the Stokes–Einstein equation. *J. Chem. Ed.* **1970**, *47*, 261–270.

(16) Scattering Length Density. http://gisaxs.com/index.php/Scattering_Length_Density.

(17) The Atomic Scattering Factor Files. http://henke.lbl.gov/optical_constants/asf.html.

(18) Glatter, O., Kratky, O., Eds. *Small Angle X-ray Scattering*; Academic Press: London, 1982.

(19) Ricker, M.; Schmidt, M. Solution properties of poly(octadecyl methacrylate) in butyl acetate, 1. Dilute Solution. *Makromol. Chem.* **1991**, *192*, 679–692.